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Bimolecular elimination reactions of cyclopentyl compounds

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BIMOLECULAR ELIMINATION REACTIONS OF CYCLOPENTYL COMPOUNDS

by

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INTRODUCTION

Preliminary investigations of four basic problems of beta elimination mechanisms are reported in this thesis.

1. The effect of changing the dihedral angle between the beta proton and the leaving group By use of the appropriately constituted cis and trans-2-arylcyclopentyl and cyclohexyl tosylates, a comparison of the ease of beta elimination as a function of the dihedral angle was undertaken. Predictions relative to the ease of beta eliminations suggest that a maximum will be approached as the dihedral angle approaches 0° and 180°, whereas a minimum will be expected at 90°. In an effort to investigate the nature of the transition state the following factors were assessed: relative rates, Hammett rho constants, deuterium isotope and solvent effects.

2. The effect of changing beta hydrogen atom's acidity The contention, that an increase in the beta proton's acidity will shift a concerted mechanism toward a carbanion transition state, was investigated. The relative rates of cis and trans-2-carbethoxycyclopentyl tosylates were compared with appropriate 2-arylcyclopentyl tosylates in order to determine whether cis and trans elimination rates tend to coalesce upon increasing the beta hydrogen's acidity.

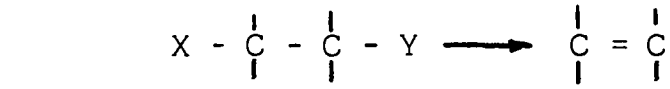
3. The relative reactivity of p-toluenesulfonate as a leaving group The relative leaving ability of the tosylate

moiety is believed to change with the amount of carbon-oxygen breaking in the transition state. The effect of a secondary alpha carbon atom on the relative leaving group ability in beta eliminations was studied by comparing the relative rates of cyclopentyl tosylate and halides to previously investigated systems containing a primary alpha carbon atom.

4. t-Butoxide-t-butanol as a base-solvent system for beta eliminations Erratic beta elimination reaction rates have stimulated a closer investigation of this base-solvent system.

HISTORICAL

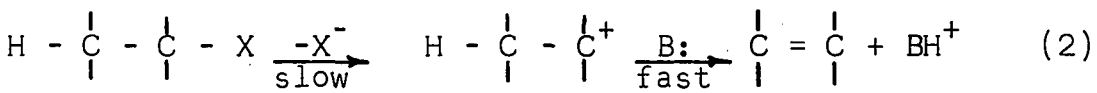
Beta eliminations are processes in which two atoms or groups are removed from adjacent carbon atoms forming a multiple bond. E.g.,



(1)

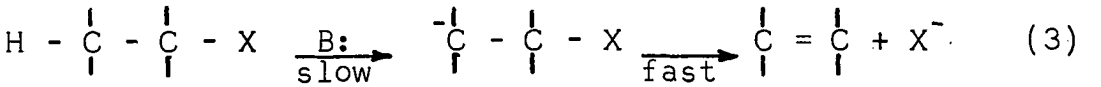
Three principal mechanisms of beta elimination have been recognized and summarized by Ingold (1) in 1950. Today, an extensive amount of data demands a modification of these original views. The recent review by Bunnett (2) states the modern theory. Ingold, Hughes and coworkers (3, 4, 5), Bishop (6), Hine (7) and Skell (8) have discussed thoroughly all but the latest literature concerning this field of elimination chemistry. It is the concern of this thesis to add only recent pertinent data and point out developments in this interesting area of research.

The E_1 or unimolecular beta elimination mechanism is the heterolytic cleavage of the C - X linkage forming a carbonium ion intermediate in the rate determining step, which then loses a beta hydrogen to solvent or base molecule.



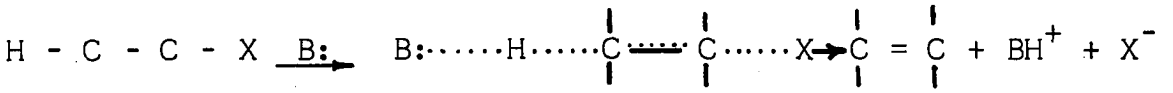
(2)

The E_{1CB} or carbanion mechanism's rate determining step is the removal of a beta hydrogen by base forming a carbanion intermediate, which in the subsequent step forms olefin with the removal of the leaving group.



(3)

In E_2 or bimolecular elimination mechanism, the beta proton and leaving group are lost simultaneously under the influence of base.



(4)

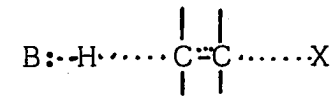
The difference in the three beta-elimination mechanisms is the extent of C - H and C - X bond breaking in the rate determining step. The E_2 mechanism in its modern interpretation encompasses the range of transition states from one extreme "nearly E_1" to the other "nearly E_{1CB}". The "nearly E_1" transition state is a synchronous mechanism approaching a carbonium ion intermediate where the C - X bond breaking is far advanced and the C - H bond is relatively undisturbed. The alpha carbon atom has a high partial positive charge. The "nearly E_{1CB}" transition state is analogous to that of "nearly E_1" except that it is the C - H bond which is almost broken with the corresponding base-hydrogen bond nearly formed and the C - X bond is only slightly stretched. The beta carbon atom has a high negative partial charge. Between these E_2 mechanistic extremes is a "central" transition state. This is the ideal synchronous transition state where the C - X and C - H bonds are half broken and the base-hydrogen bond is half formed.

It is noted by Bunnett (2) that even this broad mechanism scheme is not adequate to encompass all of the data. The double bond character of the transition state is not supplied by the mentioned mechanisms and it becomes necessary to add to all the possible transition states a diversity of double bond character. For instance, the "central" E_2 mechanism has fifty per cent double bond character. But, the C - X and C - H bonds may be broken to the extent of seventy-five per cent and the transition state would contain more double bond character. The fraction of double bond character can vary from nearly zero to nearly one. Furthermore, the amount of double bond character need not be equal to the amount of C - X or C - H bond breaking. Partial charges may reside on the alpha or beta carbon atoms instead of being delocalized over the alpha carbon-beta carbon bond. In summary, a beta elimination reaction can be placed into one of three mechanisms. If the reaction is E_2 in nature, it can be categorized as either "nearly E_1", "central" or "nearly E_{1CB}". Double bond character and/or partial charges on the alpha and beta carbon can also be described. Although the double bond character of the transition state is of interest, its influence on product ratios and relative rates of elimination reactions has not been determined.

The empirical rules of Hofmann (9) and Saytzeff (10) predict the position of the double bond in unsymmetrical elimination reaction products. The Hofmann rule, "the least

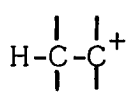
substituted olefin is the predominant product from the elimination of onium salts ($-\overset{+}{N}R_3$, $-\overset{+}{S}R_2$, $-\overset{+}{P}R_3$)" has been interpreted by Ingold (1) on the basis of electronic inductive effects. The onium's positive charge acidifies the beta protons and the most acidic proton gives rise to the predominant product. In contrast, the Saytzeff rule, "the most highly substituted olefin is the predominant product from the elimination of secondary and tertiary halides and esters," has as its product determining factor the stability of the olefinic product. The proton acidity is not pronounced enough to steer the reaction away from the most thermodynamically stable products. In summary, the two types of elimination products can be characterized by the transition state. The Saytzeff elimination has a great deal of double bond character in the transition state whereas the Hofmann reaction has very little (11).

Brown (12-17) has reasoned that steric effects of the reactant, leaving group and base cause crowding in the transition state and Hofmann or Saytzeff products are the result of steric factors. Although this approach is spectacularly different from Ingold's, both views can be rationalized by the double bond character of the transition state. The bulkier the system is, the less stability is gained by having a considerable amount of double bond character in the transition state and therefore, more Hofmann products are realized. Also, it has been noted that poor leaving groups

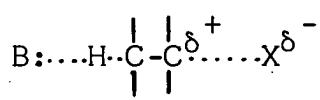


E_2 "central"

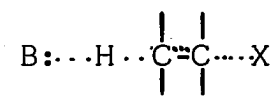
(large amount of double bond character)



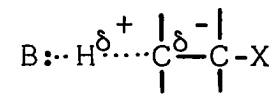
E_1



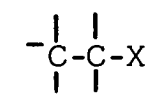
E_2 "nearly E_1"



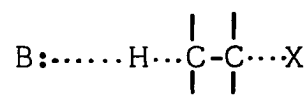
E_2 "central"



E_2 "nearly E_{1CB}"



E_{1CB}



E_2 "central"

(small amount of double bond character)

Figure 1. Transition states of beta elimination reaction mechanisms

which acidify the beta protons in the transition state lead to Hofmann products. Ledger and McKenna (18) comparing E_1 and E_2 products of 7-α-cholestanyl trimethylammonium ion concur with Brown's hypothesis that steric effects determine the product ratios and rates of these elimination reactions. On the other hand, Saunders (19) and DePuy (20, 21) have shown that E_2 rates and product ratios follow a reverse relationship to the steric size of the halogen leaving groups. Along with Banthorpe, Hughes and Ingold (4), Saunders has contended that polar effects determine the product distribution with steric control only in extremely hindered cases.

Bunnett (2) describes the multiplicity of the E_2 transition state with nine basic factors which are measured by five criteria. New data had modified his approach which is basically reproduced in this thesis. The following is a point by point discussion of how the various structural changes in the substrate or in the reaction conditions affect the E_2 transition state and its double bond character.

1. Introduction of an α-aryl substituent The "nearly E_1" transition state is favored because the aryl group will stabilize a positive charge on the alpha carbon atom. In the "central" transition state the aryl moiety stabilizes the incipient double bond by conjugation and more double bond character is realized.

2. Introduction of an α-alkyl substituent An α-alkyl group will stabilize a carbonium ion intermediate by

Table 1. Influences of diverse factors on the quality of the E_2 transition state[a]

Factor	Transition state		
	"Nearly E_1"	"central"	"Nearly E_{1CB}"
1. α-Aryl group	←	←	←
2. α-Alkyl group	←	←	←
3. Better leaving group	←	←	←
4. Leaving group more electron attracting	→	→	→
5. β-Aryl group	→	→	→
6. β-Alkyl group	←	←	←
7. Electron-attracting β-substituent	→	→	→
8. Better solvent for ions (x initially neutral, base negative)	←	←	←
9. Stronger base	?	?	?

[a]Reproduced from Bunnett (2).

an inductive effect and the mechanism is shifted toward the "nearly E_1" transition state. The double bond character of the transition state would be aided only if the alkyl group increased the C - X bond breaking by steric interference. In most cases it seems to have little influence.

3. Introduction of a better leaving group This change means a more advanced C - X bond breaking or a shift towards the "nearly E_1" transition state. The extended C - X breaking will increase the double bond character of the E_2 mechanism. This is realized by comparing the opposing "central" E_2

transition states (Figure 1).

4. Introduction of a greater electron attracting leaving group The inductive effect of the electron attracting leaving group acidifies beta hydrogen atoms and favors a beta carbanion. Also, it destabilizes any positive charge on the alpha carbon and therefore clearly favors the "nearly E_{1CB}" transition state. The increased electron attracting leaving group inhibits the spreading of electron density over the alpha and beta carbon in the transition state and, indeed, does favor Hofmann products.

5. Introduction of a β-aryl substituent This group will stabilize a carbanion and shift the transition state to "nearly E_{1CB}". In a manner analogous to the α-aryl substituent, the beta aryl moiety favors more double bond character.

6. Introduction of a β-alkyl substituent The inductive effect of the β-alkyl group would destabilize any negative charge on the beta carbon atom. The long range inductive effects would stabilize a carbonium ion intermediate at the alpha carbon. These effects favor the "nearly E_1" mechanism. The steric and/or electronic forces of the β-alkyl substituent tend to block or decrease the base-beta hydrogen attraction and therefore decrease the double bond character of a "central" type transition state.

7. Introduction of an electron-attracting β-substituent The "nearly E_{1CB}" transition state is highly favored in this case because the electron attracting β-substituent would

stabilize a carbanion on the beta carbon and destabilize positive charge on the alpha carbon. If a "central" transition state is realized the increase in C - H bond breaking, affected by the increase in the electron attracting ability of a β-substituent, would increase the double bond character of the transition state.

8. Introduction of a more polar solvent to the reaction conditions The more polar solvent favors the production of ions from neutral reactants which is the "nearly E_1" type of transition state. Better solvation of the leaving group tends to increase the C - X bond breaking in the transition state. It should be noted that trends in solvent effects are virtually unknown because a change in solvent also alters base strength and other solvation properties. It is generalized that any type of charge in the transition state is favored over a neutral transition state in a more polar solvent system. It is concluded that from this effect and the decreased aggressiveness of bases due to increased solvation reported by Winstein (22), that double bond character is not supported by a more polar solvent.

9. Introduction of a stronger base to the reaction conditions Bunnett (2) declines to predict the affect a stronger base would have on E_2 transition states because base strengths vary with solvation and mechanism. P. B. D. de la Mare and Vernon (23) discovered that sodium thiophenoxide acted ten times more effectively than sodium

phenoxide or sodium ethoxide in the elimination reaction of tertiary butyl chloride even though the latter bases were considered stronger by a factor of one thousand. Explanations point out that the nucleophilicity of the thiophenoxide ion toward carbon is greater than that of ethoxide by a factor of one hundred to one thousand. At the same time, Winstein (24) proposed the merged bimolecular substitution and elimination mechanism in order to explain the olefinic product in the Sn_2 displacement of tosylate with lithium bromide in acetone of trans-4-t-butylcyclohexyl p-toluenesulfonate. The reaction definitely was not E_1 in nature and the leaving group appeared to be in position to depart with the beta proton. Eliel (25, 26) studied the elimination of bromides and tosylates in the butyl and cyclohexyl systems with thiophenoxide and hydroxide. He concluded that the reactions were similar to the previously described merged elimination. Thiophenoxide was ten times more effective than hydroxide under identical reaction conditions. Bunnett (27) investigating the elimination of 2-chloro-2-methyl-1-phenylpropane found that thioethoxide was more than seven times faster than methoxide in the elimination reaction. Not being a proponent of the merged elimination mechanism, he (28) later stated that the order of thermodynamic affinity for hydrogen or carbon was methoxide or hydroxide greater than thiophenoxide whereas the order of kinetic reactivity toward hydrogen or carbon was thiophenoxide greater than the

alkoxide ions. Swain (29) thought the second order reaction of thiophenoxide with benzyldimethylsulfonium ion in water at 80° appears to be accelerated by ancillary molecular bonding of the complex or charge transfer type at the transition state. Recently, a conclusive set of experiments (Table 2) by Bunnett (30) shows that thioethoxide ion is more reactive than methoxide ion when E_2 eliminations are "nearly E_1" in the transition state. Winstein (31) at this time stated that the merged eliminations were really E_2 eliminations promoted by weak thermodynamic bases such as chloride and bromide ions.

Table 2. Comparison of bases CH_3O^- and $CH_3CH_2S^-$ in an E_2 elimination reaction (27, 30)

X (in decreasing leaving group ability)	Cl	$^{+}S(CH_3)_2$	$-SO_2CH_3$
$\frac{\text{rate } CH_3CH_2S^-}{\text{rate } CH_3O^-}$	6.5 to 11.4	0.79 to 0.86	~0 to 0.05
	$k_H/k_D = 2.6$ and ρ is very small.		

There are certain criteria of the E_2 mechanism which appear in the form of rate coefficients or as relative yields of two or more products.

1. X isotope effects The leaving group's isotope effect is the measurement of the amount of C - X bond breaking in the transition state. The reaction rates are measured with the element, in the leaving group bonded to the alpha carbon

atom, consisting of two isotopes. The lighter isotope reacts faster if there is any C - X bond breaking in the rate determining step. E_1 eliminations have the maximum X isotope effect. Nitrogen and sulfur in the onium ions have been the only X isotope effects measured in elimination reactions.

Colter and Johnson (32) have proposed another method for the determination of C - X bond breakage in the transition state. The Hammett rho value for p and m substituted benzenesulfonates becomes more positive as this leaving group's separation from the alpha carbon atom in the transition state increases.

2. H isotope effect A recent review by Westheimer (33) presents the modern theory of the hydrogen isotope effect (k_H/k_D). This effect is a maximum when the beta hydrogen is fifty per cent transferred from the beta carbon atom to the base. The rate ratio gradually decreases as the beta hydrogen becomes more or less transferred. If no C - H bond breaking occurs or if a carbanion intermediate is formed in the rate determining step then k_H/k_D equals one. The maximum isotope effect is believed to be seven or eight at room temperature and decreases with increasing reaction temperature.

Another type of hydrogen isotope effect has recently been put to excellent use in beta elimination chemistry by Thornton (34). Reaction rates are measured using hydroxide-water and deuteroxide-deuterium oxide as the base solvent systems. The relative amount of C - H bond breaking of two

or more substrates can be ascertained by comparing their respective isotope rate ratios $k\ OD^-/D_2O \,/\, k\ OH^-/H_2O$. The greater the isotope rate ratio the more tightly the beta proton is attached to the oxygen atom of the base. This type of evidence can supplement primary hydrogen isotope measurements and conclusions drawn from other isotope data.

3. The stereoelectric preference of E_2 elimination reactions Early investigations summarized by Bunnett (2), Hine (35), Cram (36) and Barton (37) showed that trans elimination of H and X was favored over cis elimination and the transition state geometry was anticoplanar. DePuy and coworkers (38) have pointed out that the ease of E_2 eliminations may vary with the dihedral angle between H and X. A plot of the rate of elimination of a given system versus the dihedral angle between the leaving group and proton is predicted to show a maximum at both 0° (cis coplanar) and 180° (trans anticoplanar) and a minimum at 90°. Elimination transition states in which H and X atoms cannot assume a coplanar or anticoplanar arrangement are not only slower but may proceed by one of the extreme mechanism such as E_{1CB} or "nearly E_{1CB}".

4. Eclipsing effect Product and rate ratios are subject to the relative stability of the transition states. The most stable transition state will contain the fewest interactions between alpha and beta carbon substituents. "E_1 and E_{1CB}" like beta elimination processes sacrifice antiperiplanarity for a sterically less encumbered transition state.

Cram (39), Sicher (40) and Papathanassiou (41) have published examples of this phenomenon.

5. Effects of β-substituents The Hammett rho value gives an indication of the amount of negative charge on the beta carbon atom in the transition state of an elimination reaction. Rho is evaluated from rate measurements of meta and para substituted aryl substituents using the Hammett (42) equation. As the carbanion character of the beta carbon atom increases, the rho value increases. The maximum value of rho may be approximately five which Szwarc (43) measured for the living polystyrene anionic homo- and copolymerization in tetrahydrofuran. Rho values decrease with increasing reaction temperature.

E_1 reactions have a carbonium ion intermediate which loses a proton to form Saytzeff products. The solvolysis of 2-chloro-2-methylbutane (44) in eighty per cent aqueous ethanol to give a thirty-six per cent yield of olefinic products is an example of such a reaction. Eighty per cent of the E_1 products is the internal olefin. The k_H/k_D is 1.8 which agrees well with the value reported by Silver (45) for the E_1 elimination of t-pentyl chloride and Winstein's (46) values for Sn_1 reactions. It is noted that E_1 reactions are accompanied by Sn_1 reactions.

The "nearly E_1" E_2 mechanism has been the subject of many recent investigations. Research concerning the strength of bases has been described previously. In close connection

with that work has been studies concerning abnormal product ratios of E_1 reactions. Abnormal ratios of Saytzeff to Hofmann products have been reported by Smith (47) and Cristol (48) for E_1 reactions. For the solvolysis of cis and trans-2-phenylcyclohexyl p-toluenesulfonates, Cristol found that the trans compound gave predominantly the Hofmann product (3-phenylcyclohexene) whereas the cis compound via the same carbonium ion intermediate gave almost all 1-phenylcyclohexene. The ratio of products was dependent upon the leaving group. Cram (49) observing similar results with an acyclic system suggested the increase in Hofmann type products was due to the leaving group remaining associated with the carbonium ion long enough to effect seriously the behavior of that ion and in some cases the anion abstracts a proton from the carbonium ion to form the external olefin. Winstein (50) suggested that ion pairs are involved in the intermediate carbonium ion and are responsible for the change in products with a change in leaving group. Complete inversion of configuration was found when 2-octyl p-toluenesulfonate was solvolyzed in glacial acetic acid. Ion pairs were suggested by Streitwieser (51) to account for the stereochemistry of this Sn_1 product. Solvolysis of erythro and threo-2-deutero-3-tosyloxybutane showed a stereochemical preference for elimination. In this work, Skell (52) found that cis elimination was occurring in protic solvents by the removal of the beta proton by the parting p-toluenesulfonate

group which must remain on the same face of the carbonium ion until it has accomplished this removal. By contrast, trans elimination occurred in more basic solvents requiring attack by the solvent from the antiperiplanar position or essentially like the concerted E_2 elimination. The difference between E_2 and E_1 in basic solvents may only be a matter of degree of polarization of the C - X bond. Skell states that ion pairs do not play major roles in these solvolytic eliminations.

The participation of solvent in E_2 eliminations is difficult to ascertain. The work concerned with thiophenoxide promoted E_2 eliminations and the above described "nearly E_1" eliminations are very similar. A third type of elimination system is apparently in this category of "nearly E_1" transition state with possible anchimeric proton removal by the leaving group. Cis and trans-1, 2-dichlorocyclohexane was subjected to refluxing quinoline. Stevens (53) found normal E_2 trans elimination greatly favored over the cis elimination. But, Saunders (54) found unexpected results when cis and trans-2-trimethylammonium or tosyloxymethylcyclohexanes were refluxed with pyridine. The normal trans elimination was greatly favored over the cis elimination using hydroxide, ethoxide or t-butoxide as bases but there was little stereospecificity in refluxing pyridine. The cyclopentyl analogs were even less stereospecific and Saunders concluded that pyridine promoted the E_1 mechanism.

Table 3. Dehydrohalogenation of cis and trans ethylenes to form acetylenes

Compounds	Base/solvent	Elimination Type	Rel. Rate[a]	E_a Kcal./mole	$\Delta S^{\ddagger}$ (e.u.)	Ref.
ClHC = CHCl	$^{-}OCH_3/CH_3OH$	trans	300	35.1	22	56
		cis	1	29.0	-12	
BrHC = CHBr	$^{-}OCH_3/CH_3OH$	trans	4×10^5	28.1	16	56
		cis	8	33.4	5	
		$\frac{\text{trans } E_2}{\text{cis } E_2} = 5 \times 10^4$				
	$^{-}OCH_3/CH_3OH$	cis $k_H/k_D = 1.03$				57
		Hydrogen exchange is twenty-five times faster than elimination				
IHC = CHI	$^{-}OCH_3/CH_3OH$	trans	3×10^7	24.7	14	56
		cis	285	35.8	24	
		$\frac{\text{trans } E_2}{\text{cis } E_2} = 3 \times 10^5$				
$C_6H_5HC = CHBr$	$OH^{-}/CH_3\overset{OH}{\overset{\vert}{C}}HCH_3$	trans	5×10^4	21.1	-5.6	58
		cis	1	31.8	4.0	
$C_6H_5HC = CClC_6H_5$						
	OH^{-}/CH_3CH_2OH	trans	200	28.1	5.6	59
		cis	1	33.7	1.0	

[a]Relative rates applied to only those substances which are structurely similar measured under identical reaction conditions. This applies to all subsequent tables.

Levisalles (55) using a steriod found that the cis elimination of p-toluenesulfonate was greatly favored in boiling collidine when the p-toluenesulfonate group was in an equatorial position. Trans elimination was only slightly favored when the tosylate was in an axial position. The "nearly E_1" transition state with the p-toluenesulfonate group assisting the removal of the beta hydrogen might account for these results.

The E_{1CB} mechanism has been the subject of many investigations since Cristol's (60-62) work on β-hexachlorobenzene. This study and subsequent observations concerning carbanion intermediates have been reviewed by Hine (35) Skell (8) and Bishop (6). Ideally, the carbanion intermediate is shown by hydrogen or deuterium exchange with the solvent. Deuterium exchange is not a necessary condition for a carbanion intermediate in an elimination reaction because the carbanion may react to give products at a rate much greater than the rate of reprotonation. In the elimination of substituted ethylenes to acetylenes (Table 3) Miller (56) has observed that a rate of hydrogen exchange is twenty-five times faster than the rate of elimination. A k_H/k_D equal to 1.03 was found because hydrogen was exchanged for deuterium before elimination occurred.

Hine (63, 64) noted that the elimination of 1, 1, 1-trifluoro-2, 2-dichloroethane with methoxide proceeded through a carbanion intermediate because the rate of deuterium exchange was faster than the rate of elimination. The

carbanion intermediate was stabilized by the electron attracting halogen atoms. There are many publications concerning the E_{1CB} mechanism but there is only Hine's case where the mechanism has been substantiated by deuterium exchange. Since Bishop's (6) and Hine's (35) reviews, Cristol (65, 66), Papathanassiou (41) and Bordwell (67, 68) have published papers on the E_{1CB} mechanism. Bordwell's system is particularly interesting because of his previous stand against carbanion intermediates in elimination reactions. The cis elimination of 1-phenyl-1-acetoxy-2-nitrocyclohexane is four times faster than the trans elimination in piperidine, chloroform and ethanol. The Hammett rho value for the alpha carbon atom is +1.45, k_H/k_D equals 4.9, the thermodynamic activation parameters and the salt effects are the same for both eliminations. The difference in rate is due to the steric hindrance of carbanion formation by base attack and the steric assistance of a planar nitro substituted carbanion. Bordwell concludes that this system is the first in which both cis and trans eliminations occur via a carbanion intermediate. The author of this thesis finds the data does not unquestionably lead to a carbanion mechanism. The rho value cannot be compared with other values especially with that of a known E_2 process. The same rho values for both cis and trans eliminations are a common occurrence in cyclic compounds (Table 5). Anchimeric assistance of beta hydrogen removal by the acetate group is possible according to Curtin (69). It

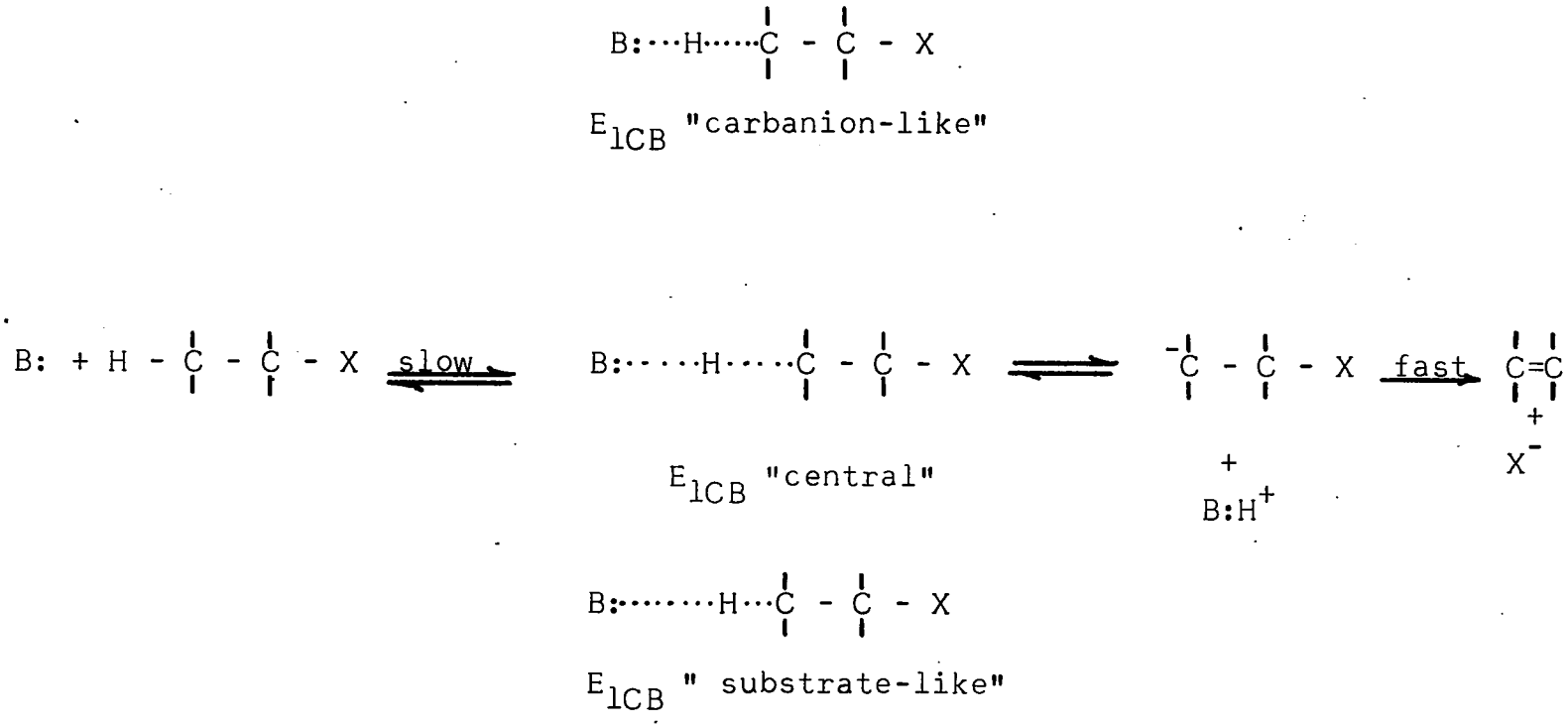


Figure 2. Transition states of the E_{1CB} reaction mechanism

is suggested that other esters be used as leaving groups particularly the sterically encumbered triethylbenzoate which could not participate anchimerically in the elimination reaction.

The problem of placing a particular reaction in the E_2 or E_{1CB} mechanism is extremely difficult. Previously, the E_2 spectrum of transition states has been described in relation to structural and electronic changes of the substrate and to mechanistic criteria (i.e. Hammett rho correlations and deuterium isotope effects). It would seem that the "pure" E_{1CB} mechanism could be described by the same criteria which describe the "nearly E_{1CB}" transition state. This supposition is false because the transition state in the rate determining step of the E_{1CB} mechanism has different criteria than those of the intermediate carbanion. The only criteria proving the existence of a carbanion intermediate in beta elimination reactions is hydrogen-deuterium exchange. But, the criteria which described the E_{1CB} range of transition states are identical in every respect to the E_2 criteria discussed earlier except the isotope effect involving the leaving group must be negligible. This same isotope effect is also very small for the E_2 "nearly E_{1CB}" mechanism. The k_H/k_D and Hammett rho-values varied from their respective maximum to minimums as they did in the corresponding E_2 transition states. Figure 2 shows the different amounts of carbanion character on the beta carbon atom and carbon-hydrogen bond breaking. The spectrum

of E_{1CB} transition states depends on the relative acidity of the beta proton and the attacking base. Since the carbanion is produced by the action of a base on an acid in an equilibrium process, the amount of proton bond breaking depends on the beta hydrogen's acidity and the base's strength. If the proton is weakly acidic and the base is weak, the transition state will be near the product of the acid-base equilibrium, the carbanion. The ρ would have a high value and k_H/k_D would be small because the proton would be 90% or more transferred in the transition state. A very acidic beta proton reacting with a strong base would, in the acid-base equilibria, favor a substrate-like transition state with a low ρ-value and low k_H/k_D value. The range of transition states covers all the intermediate possibilities analogous to the E_2 transition state spectrum. This hypothesis has some experimental evidence in the field of carbanion chemistry. Hine (7) stated that carbanions do not react with proton as readily as they undergo most other reactions. The beta eliminations involving an acidic beta proton could react via a carbanion intermediate yet show no hydrogen-deuterium exchange. Another type of carbanion reaction, the aldol condensation (Equation 5), also shows no deuterium exchange unless the reaction is carried out in very dilute solutions (70). The carbanion, once formed reacts faster with another aldehyde molecule than it does with deuterium oxide. It is felt that this intermolecular reaction is much less favorable than the intramolecular elimina-

tion of halides or p-toluenesulfonate in the E_{1CB} elimination mechanism.

$$CH_3C(=O) - H \xrightarrow[D_2O]{OD^-} CH_3\overset{OD}{C}HCH_2\overset{O}{C} - H \qquad (5)$$

Wiberg (71) has evidence for a reverse isotope effect for a carbanion reacting with equimolar mixture of methanol and deuteromethanol. A deuterium isotope effect of 0.96 was found

$$C_6H_5CH_2^- + \begin{matrix} CH_3OH \\ CH_3OH \end{matrix} \longrightarrow \begin{matrix} C_6H_5CH_3 \\ C_6H_5CH_2D \end{matrix} + CH_3O^- \qquad (6)$$

and by the principle of microscopic reversibility, the deuterium isotope effect for the reverse reaction is also approximately unity (Equation 7).

$$\begin{matrix} C_6H_5CH_3 \\ C_6H_5CH_2D \end{matrix} + CH_3O^- \longrightarrow C_6H_5CH_2^- + \begin{matrix} CH_3OH \\ CH_3OD \end{matrix} \qquad (7)$$

Equation 7 is very similar to the E_{1CB} beta elimination reaction (Equation 3). According to the theory of E_{1CB} transition states, k_H/k_D is predicted to be very close to unity because the hydrogen removed is not acidic and the base is relatively weak for the task for which it is required to perform. The energy profile diagram of Equation 7 would disclose that the transition state is very close to the carbanion product. The products are very unstable relative to the reactants and a large amount of energy must be applied

Table 4. E_2 elimination of beta phenylethyl substances to styrene

X	Base/solvent	Rel. Rate	ρ[a]	k_H/k_D[a]	E_a (Kcal./ mole)	$\Delta S^{\ddagger}$	Ref.[b]
F	$CH_3CH_2O^-/CH_3CH_2OH$	1	3.12	--	25.3	-5.4	6,20
Cl	30°C.	70	2.61	--	23.2	-5.6	21,72
oTos[c]		400	2.50[d] (2.15)(73)	5.66(73)	20.4 19.6(74)	11.2 -9.2(74)	
Br[e,f,g]		4,300	2.14	7.11(73)	20.4(73)	-6.8(73)	
I		28,000	2.07 (2.64)(74)	--	13.2 (23.3)(74)	-23.8 (7.7)(74)	
$^+S(CH_3)_2$		40,000[h]	2.75	5.07(73)	23.9 (25°C.)	7.7 (25°C.)(73)	

[a]Rho and k_H/k_D values were measured at 30°C. unless otherwise specified.

[b]References 6, 20, 21 and 72 are the sources of any data except where otherwise specified.

[c]oTos = p-Toluenesulfonate.

[d]Rho is 2.04 if p-methoxyaryl compound's rate is taken into consideration (20).

[e]$k_H/k_{D_{CH_3}}$ = 1.17 on the alpha carbon atom (75).

[f]$C_6H_5\text{-}CH\overset{CH_3}{CH_2}Br$ k_H/k_D = 7.5. The rate is less than that of the beta phenylethylbromide (76).

[g]No deuterium exchange (77).

[h]Extrapolated from data at other temperatures.

Table 4. (Continued)

X	Base/solvent	Rel. Rate	ρ	k_H/k_D	E_a (Kcal./ mole)	$\Delta S^{\ddagger}$ (e.u.)	Ref.
$^{+}N(CH_3)_3$ [a,b]		--	3.77(2)	2.98 (50°C.)			
Cl	OH^-/H_2O [c]	--	1.65	--	24.8 (60°C.) [d]	--	80
					(24.8)	(-1.9)	81
$^{+}S(CH_3)_2$ [e,f,g]	30°C.	--	2.21(74)	--	24.0	-4.2	82

[a] Nitrogen isotope effect is approximately 30% of the calculated maximum at 60°C. (78).

[b] Deuterium exchange has been noted in beta phenylethyltrimethylammonium ion with ethoxide and deuteroethanol (79).

[c] Approximately 0.001 times the rate in ethanol (82).

[d] 67% aqueous ethanol.

[e] Sulfur isotope effect is approximately 10% relative to the maximum calculated value and the measured value of t-butyl dimethylsulfonium ion hydrolysis (81).

[f] $k_{\frac{OD^-}{D_2O}} / k_{\frac{OH^-}{H_2O}} = 1.57$ at 80°C. (34).

[g] No deuterium exchange or ylide or α-β elimination mechanisms found (83).

Table 4. (Continued)

X	Base/solvent	Rel. Rate	ρ	k_H/k_D	E_a (Kcal./ mole)	$\Delta S^{\ddagger}$ (e.u.)	Ref.
$^{+}N(CH_3)_3$	[a,b,c]	--	--[d]	--	25.5 (25°C.)	3.7[e] (48) (25°C.)	
Cl	$\underline{t}$-BuO^-/t-BuOH	1					
oTos	30°C.	6 (50)[f]	3.39	8.01(73)	14.7	-25.2	
Br		25	2.08	7.98(73)	13.0	-25.0	
I		130	1.88		13.2	-23.8	
oTos	$^-OCH_2CH_3/\underline{t}$-BuOH	1(11)[g]	2.60	--	15.8	-18.7	
Br		6	2.28	--	13.8	-25.0	
I		27	2.07	--	--	--	

[a]Nitrogen isotope effect is reported to be 0% of theoretical value (84).

[b]$k_{\frac{OD^-}{D_2O}} / k_{\frac{OH^-}{H_2O}} = 1.79$ at 80°C. (34).

[c]Optically active α-phenylethyltrimethylammonium ion is quantitatively recovered unracemized after 100 hours at 81°C. No ylide or carbanion mechanism was involved in the β-phenylethyltrimethylammonium ion (85).

[d]An appreciable tritium isotope effect found (85).

[e]93% aqueous ethanol.

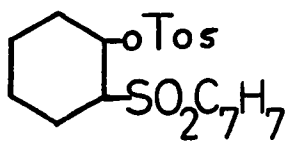
[f]52 times faster than the rate in ethanol.

[g]11 times faster than the rate in ethanol.

to the reactants in order to form products. Although the evidence is meager, the indications point to the conclusion that there is not a clear line of demarkation between the E_{1CB} and E_2 transition states. The E_{1CB} carbanion-like transition state merges with the E_2 "nearly E_{1CB}" transition state. At this time there is a wide gap between the experimental data on beta elimination reactions and the theories of their transition states and mechanisms.

Bunnett (2) has discussed this tabulated data (Table 4) in relation to the modern theory. There is additional evidence that the beta phenylethyl system is mechanistically on the "nearly E_{1CB}" side of the "central" transition state. Thornton (34) stated that the relative values of a secondary isotope effect $k_{\frac{OD^-}{D_2O}} / k_{\frac{OH^-}{H_2O}}$ showed the beta hydrogen to be more tightly attached to the oxygen of the base in the trimethylammonium transition state than in the dimethylsulfoium transition state. This is supplementary evidence to rho values and the primary isotope effect which places the ammoium ion more toward the E_{1CB} extreme of the spectrum of E_2 transition states. Banthorpe (79) has evidence of a possible carbanion intermediate in the same ammonium ion. His results show a great deal of deuterium exchange which is the primary evidence for the carbanion mechanism. The data, however, is questionable because it is in direct conflict with results published by Doering (85). Banthorpe claims that the alpha phenylethyltrimethylammonium ion exchanges with

Table 5. E_2 eliminations of <u>cis</u> and <u>trans</u> cyclohexane derivatives

Compound	Base/solvent	Rel. Rate	$\frac{k\ trans}{k\ cis}$	E_a[a] (Kcal./ mole)	$\Delta S^{\ddagger}$ (e.u.)	Ref.
B-hexachloro-benzene	OH^-/H_2O	--	7,000-24,000	a	b	60-62
$CH_3CH_2O^-$/70% 30%	CH_3CH_2OD CH_3CH_2OH	After one half life 1 out of every 150 molecules remaining contained deuterium				
	OH^-/70% aq. dioxane	--	--	trans (17.4)(87)	-7.6(87)	88
	OH^-/50%[c,d] aq. dioxane	--	400	trans (17.5)(89) trans (25.2)	-- -5.3(89)[e]	

[a] 9-13 Kcal. higher than the other hexachlorobenzene isomers. (cis)

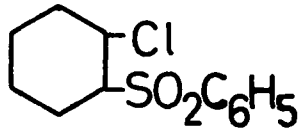
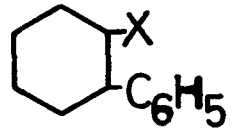
[b] Cis elimination makes $\Delta S^{\ddagger}$ more positive. (trans)

[c] Rho is the same for both cis and trans eliminations also the leaving group effect the rate in the same ratio for both eliminations. General base catalysis was observed. The leaving group has very little effect on the rate (90). (cis)

[d] Cis elimination was 10^3-10^5 times faster than deuterium exchange (89). (cis)

[e] Deuterium exchange parameters.

Table 5. (Continued)

Compound	Base/solvent	Rel. Rate	$\frac{k\ trans}{k\ cis}$	E_a (kcal./mole)	$\Delta S^{\ddagger}$ (e.u.)	Ref.
	$(CH_3)_3N$	--	25	--	--	
	$(CH_3CH_2)_3N$	--	100	--	--	
	OH^-/80% aq. CH_3CH_2OH	--[a]	490	trans 15.7 10^4(37)[b]	--	91
 X = cis oTos	OH^-/93% aq. CH_3CH_2OH	2×10^4		22.4	-6.4	48

[a]Rate is 10^9 faster than the rate of cyclohexyl chloride. The rho value is +1.42 and the same for both cis and trans eliminations.

[b]$\underline{t}$-BuO^-/$\underline{t}$-BuOH.

Table 5. (Continued)

Compound	Base/solvent	Rel. Rate	$\frac{k\ trans}{k\ cis}$	E_a (Kcal./ mole)	$\Delta S^{\ddagger}$ (e.u.)	Ref.
X = cis $\overset{+}{N}(CH_3)_3$	[a,b,c,d]	135	135	30.3	11.2	48
X = trans $\overset{+}{N}(CH_3)_3$		1		33.4	11.9	48
X = cis $\overset{+}{S}(CH_3)_2$		10^6	400	24.3	8.7	48
X = trans $\overset{+}{S}(CH_3)_2$		2.5×10^3		33.8	28.8	48
$C_6H_5CH_2CH_2\overset{+}{N}(CH_3)_3$		10^4		25.5	3.7	48
$C_6H_5CH_2CH_2\overset{+}{S}(CH_3)_2$	$CH_3CH_2O^-/CH_3CH_2OH$	10^6		23.9	7.7	48, 74
$C_6H_5CH_2CH_2$oTos		2×10^4				72

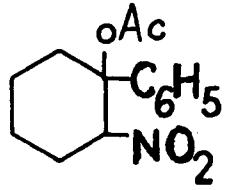
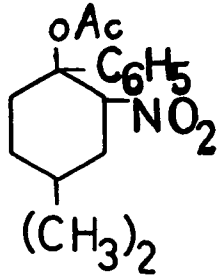
[a]Nitrogen isotope effect of about 5% of calculated maximum (92, 93).

[b]Nitrogen isotope effect of about 30% of calculated maximum (92, 92).

[c] $k_H/k_D = 5.8$ (92).

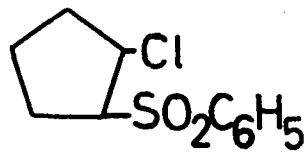
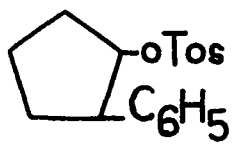
[d]No epimerization (94) or deuterium exchange (92) or ylide formation noticed (94).

Table 5. (Continued)

Compound	Base/solvent	Rel. Rate	k trans / k cis	E_a (Kcal./ mole)	$\Delta S^{\ddagger}$ (e.u.)	Ref.
	$C_5H_{10}NH/CHCl_3$- CH_3CH_2OH	--	0.25	6.9	-50	67, 68
	Rho = +1.45 for alpha carbon atom					
	k_H/k_D = 4.9					
	4-t-Butyl group has no effect on rate of cis or trans elimination.					
	Addition of 0.1M. LiBr or $(Bu)_4N^+I^-$ doubles rate in both eliminations.					
	$C_5H_{10}NH/CHCl_3$-CH_3CH_2OH	--	0.13[a]	--	--	67, 68

[a]Cis elimination 5 times the rate of cis elimination without the methyl groups.

Table 6. E_2 elimination of cis and trans cyclopentane derivatives

Compound	Base/solvent	Rel. Rate	k trans / k cis	E_a (Kcal./ mole)	$\Delta S^{\ddagger}$ (e.u.)	Ref.
	OH^-/50% aq. dioxane	--[a]	20[b]	trans 15.7(89)	--(89) -4.9[c]	88,95 96
	$(CH_3)_3N$	--	1.2	trans 11.8 cis 12.1	-26.4(97) -27.2(97)	
	$(CH_3CH_2)_3N$	--	7			
	OH^-/50% aq. CH_3CH_3OH	-- --	40	--	--	91
	t-BuO^-/t-BuOH	--	14	--	--	38
	Rho equals +2.34 for cis elimination					

[a]Trans elimination 1/4 the rate of $C_7H_7SO_2CH_2\overset{oTos}{C}HCH_3$ with OH^- in 50% aq. dioxane and 1/10 the rate of this compound in the other two bases.

[b]Cis elimination was 10^3-10^5 times faster than deuterium exchange (90).

[c]Deuterium exchange parameters.

ethoxide deuteroethanol like the beta analog but Doering finds the same compound, optically active, does not racemize under similar conditions. The location of the members of the beta phenylethyl compounds in the transition state spectrum is not exactly known but, in spite of Banthorpe's recent results, the compounds are placed between the "central" and the "nearly E_{1CB}" transition states in order of increasing carbanionic character I, Br, oTos, Cl, $\overset{+}{S}(CH_3)_2$, F and $\overset{+}{N}(CH_3)_3$.

Cyclic structures (Tables 5 and 6) have been investigated in order to elucidate the E_{1CB} mechanism ever since Cristol (60-62) proposed such a mechanism for the base catalyzed elimination of β-hexachlorohenzene. The difference in rates of cis and trans elimination has been of special interest. In some cases, cis elimination have been described by the E_{1CB} mechanism although the data does not entirely collaborate this mechanism. DePuy and coworkers (98) presented the hypothesis that the cis eliminations of trans-2-phenyl-cyclohexyl and pentyl p-toluenesulfonates are concerted E_2 processes. This may be generally valid for all the cyclic systems with an activated beta hydrogen atom. The cis elimination of trans-2-phenylcyclohexyltrimethylammonium ion appears on the "nearly E_{1CB}" side of the "central" transition state. The small nitrogen isotope effect means almost no C - N bond breaking in the rate determining step. A k_H/k_D of 5.8 shows that the beta hydrogen is probably more strongly bonded to the base than to the beta carbon atom in

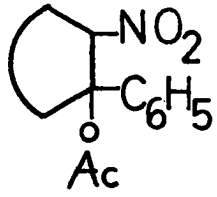
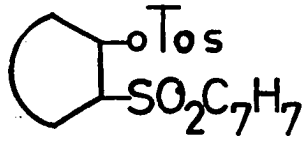
the transition state. The rho constants measured for only two compounds are consistent with a concerted carbanion-like process.

Bordwell (88), using the criteria of general base catalysis, concluded that if a carbanion were formed it would have a lifetime of less than 10^{-8} seconds. Skell (8) found that if a carbanion formed it did not rotate but remained asymmetric. He concluded that the carbanion lifetime was less than 10^{-9} seconds. These results only apply when the carbanion intermediate loses a proton slower than reprotonation of the anion.

The effect of ring size on elimination reactions (Table 7) is an effect of stereochemistry of each particular ring. It is difficult to note any trend with differing ring sizes because the conformation of these rings is not clearly known at the present time. Bordwell (68) thought the rate increase from 6, 5 to 4 membered rings is due to steric hindrance and steric assistance of carbanion formation. DePuy (98), noting the same type of phenomenon in a different system, interpreted the increasing rates of cis eliminations, 6 to 5 membered rings, as added evidence that the mechanism is concerted and coplanar. This hypothesis accounts for the large rate increases in cis eliminations and the relatively small rate increase for trans eliminations from six to five membered rings.

The norbornyl dichloride (Table 8) was the first case of

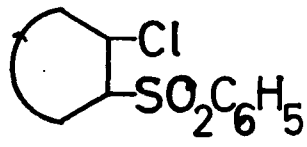
Table 7. The effect of ring size on beta elimination reactions

Compound	Elimination Type	Base/solvent	k_4	k_5	k_6	k_7	Ref.
	cis	$C_5H_{10}NH/CHCl_3$	--	97	0.45	0.72[a]	68
	trans	CH_3CH_2OH	1150	--	0.13	0.23	
	cis	OH^-/50% aq. dioxane	--	60	1	--[b]	88
		OH^-/70% aq. dioxane	--	120	1	--	
		$(CH_3)_3N$	--	100	1	--	
		$(CH_3CH_2)_3N$	--	120	1	--	
	trans	OH^-/50% aq. dioxane	--	3	1	--	
		$(CH_3)_3N$	--	5	1	--	
		$(CH_3CH_2)_3N$	--	7	1	--	

[a]Relative rate of 1 was assigned to erythro-2-acetoxy-3-nitro-2-phenylbutane under identical conditions.

[b]The relative rate of 1 was assigned to the six-membered ring compound in each of the following ratios.

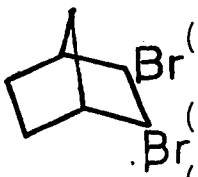
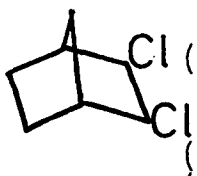
Table 7. (Continued)

Compound	Elimination Type	Base/solvent	k_4	k_5	k_6	k_7	Ref.
	cis	OH^-/80% aq.	--	31	1	--	91
	trans	CH_3CH_2OH	--	2.5	1	--	
	Solvolysis	CH_3COOH	11	14	1	25[a]	99, 100
	Solvolysis	CH_3CH_2OH	--	38	1	--[b]	101, 102

[a]Eight to 17-membered rings also have solvolysis rates listed in this reference.

[b]E_a = 23.7 Kcal./mole and $\Delta S^{\ddagger}$ = -6.4 e.u. for the solvolysis of the five membered ring compound.

Table 8. Beta eliminations of bicyclic systems

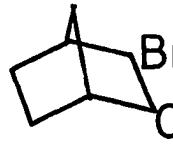
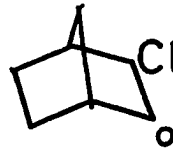
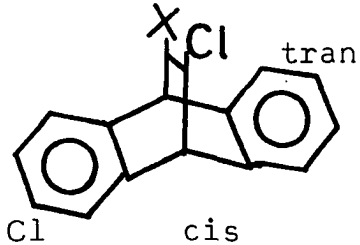
Compound	Type of Elimination	Base/solvent	Rel. Rate	E_a (Kcal./mole)	$\Delta S^{\ddagger}$ (e.u.)	Ref.
	trans (endo H-exo Br)[a]	pentoxide pentanol	1	26.2	-8.8	103
	trans (exo H-endo Br)		2.8	25.9	-7.5	
	cis (endo H-endo Br) or (exo H-exo Br)		85.9	26.4	+0.7	
	trans[b] (endo H-exo Br)	t-amyloxide t-amylalcohol	1.8	20.2	-19	
	cis[c] (endo H-endo Br) or (exo H-exo Br)		2.8	21.2	-11	
	trans (exo H-endo Cl)	pentoxide pentanol	0.02(1)	(104)30.3(32)(104)	-5.4	
	cis (endo H-endo Cl) or (exo H-exo Cl)		1.6(85)	(104)30.9(31)(104)	+4.4	

[a] Hydrogen and leaving group which are removed.

[b] $k_H/k_D = 3.4$

[c] $k_H/k_D = 3.6$

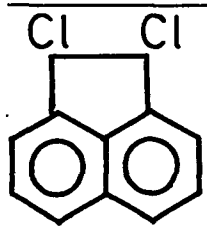
Table 8. (Continued)

Compound	Type of Elimination	Base/solvent	Rel. Rate	E_a (Kcal./mole)	$\Delta S^{\ddagger}$ (e.u.)	Ref.
	trans (exo H-endo Br only)		0.95	24.4	-13.9	
	cis (exo H-exo Br only)		27.6	25.3	-4.7	
	cis (exo H-exo oTos)		3×10^{9}(104)	19(104)		
$SO_2C_7H_7$ 	cis[a]	OH^-/50:50 dioxane	10^{10}	15.6	--	105
	trans[b]	CH_3CH_2OH	3×10^{10}	16.3		106
Cl	cis		1	26.5	-11.2	105, 106
	trans		8	30.6	3.2	

[a]Dihedral angle = 0°.

[b]Dihedral angle ≅ 110°.

Table 8. (Continued)

Compound	Type of Elimination	Base/solvent	Rel. Rate	E_a (Kcal./mole)	$\wedge S^{\ddagger}$ (e.u.)	Ref.
	cis		1	24.8	6.9	107
	trans		740	20.8	6 9	

a cis elimination being faster than a trans elimination. Although at first the cis elimination was thought to proceed via a carbanion intermediate, LeBel (103) has shown rather conclusively that the reaction is a concerted process with "nearly E_{1CB}" properties. The dehydrobromination rather than dehydrochlorination of the trans-1-bromo-2-chloronorborane argues against carbanion formation. Previous investigations by Hine (108) showed that beta halogens stabilize a carbanion in order of Cl > Br > I and an alpha halogen in an opposite order of I > Br > Cl > F. Both orders of stability would favor loss of hydrogen chloride rather than hydrogen bromide if a carbanion were an intermediate. The high value of k_H/k_D (3.4 at 127°) for LeBel's (103) eliminations and that of β-phenylethyl tosylate and the high value of ρ=3.39 (β-phenylethyl tosylate at 30°) are taken as proof of a concerted elimination with the transition state past the "central E_2" state. LeBel also noted that the stronger base increases the rate of elimination and depresses the difference between cis and trans elimination rates. The mechanistic interpretations of such effects are vague at this time.

Aliphatic compounds (Table 9a) have usually been used to show that base-catalyzed beta eliminations go stereo-specifically in a trans antiperiplanar direction and concertedly. Ethyl trimethylammonium ion and isopropyl bromide elimination reactions appear to have the "central" transition state. Brown (109) concluded that the t-amyl system underwent a concerted elimination and that the E_{1CB} mechanism was not likely to participate

because chloride should stabilize a carbanion more than a bromide or iodide. The rates were the reverse of that order.

A "nearly E_{1CB}" transition state was predicted for 1, 1-difluoro 2, 2, 2-trichloroethane because the rate of elimination was faster than the rate of deuterium exchange of 1, 1, 1-trifluoro 2, 2-dichloroethane which does undergo elimination with methoxide in methanol via an E_{1CB} mechanism. Cristol's (110) threo-2-p-toluenesulfonyl-p-chloro-2, 2-diphenylethane certainly approaches the E_{1CB} mechanism with its very acidic beta proton but lacks direct evidence of having a carbanion intermediate. The reaction is very similar to the bicyclic system in Table 8 and cyclic system in Table 6 neither of which have been proven E_{1CB} nor "nearly E_{1CB}". Sicher (40) has evoked the E_{1CB} or "E_{1CB}-like" mechanism for the beta elimination reactions of 5-substituted nonanes to explained different products ratios with different bases and/or different leaving groups. The "E_{1CB}-like" process gives a high percentage of cis olefin because it sacrifices antiperiplanarity for a sterically less encumbered transition state. This system may be sterically similar (Figure 3) to that of Cristol.

Bunnett's (27) system, discussed before in relation to base strengths, is clearly "nearly E_1" mechanistically. The small rho constant and k_H/k_D value leave little doubt when compared with the same parameters of the beta phenylethyl system (Table 4).

Table 9a. Beta elimination data of various acyclic systems

Compound	Base/solvent	Rel. rate, k_H/k_D and ρ	E_a (Kcal./mole)	$\Delta S^{\ddagger}$ (e.u.)	Ref.
t-amyl-X Cl	t-BuO^-/t-BuOH	1	--	--	109
Br		60	--	--	
I		400	--	--	
$CH_3CH_2\overset{+}{N}(CH_3)_3$ [a,b]	No carbanion mechanism but trans E_2 ethylene glycolate / ethylene glycol	k_H/k_D = 3.7	137°C.		76
$C_6H_5CHCH_2Br$ (CH$_3$)		k_H/k_D = 2.8			
	$CH_3CH_2O^-/CH_3CH_2OH$	k_H/k_D = 7.5 (25°C.)			
$^-OOC\text{-}CH(NH_2)\text{-}CH_2PO_4^=$	OH^-/H_2O 100°C.	k_H/k_D [c] = 1.85	22.2	-18.7	111

[a] Nitrogen isotope effect is about 50% of the maximum calculated value. Base-solvent was ethoxide-ethanol.

[b] n-Butyl, i-propyl and t-butyl trimethylammonium ion do not exchange with ethylene glycol- at 137°C. (79).

[c] k_H/k_D calculated maximum at 100°C. = 4.7.

Table 9a. (Continued)

Compound	Base/solvent	Rel. rate, k_H/k_D and ρ	E_a (Kcal./ mole)	$\Delta S^{\ddagger}$ (e.u.)	Ref.
$C_6H_5CH_2C(CH_3)_2Cl$	CH_3O^-/CH_3OH	k_H/k_D = 2.6 Rho is small	--	--	27
$CH_3CH_2CH_2CH(OSO_2C_6H_5)CH_3$	$CH_3CH_2O^-/CH_3CH_2OH$	Rho = +1.35	--	--	32
$C_6H_5CHClCHClC_6H_5$ meso	OH^-/95% ethanol	1	23.6	-1	110
dl		9	19.4	-10	
$C_6H_5CH(Cl)CH(SO_2C_7H_7)C_6H_5$ erythro		very fast			66
threo[a]		fast			41

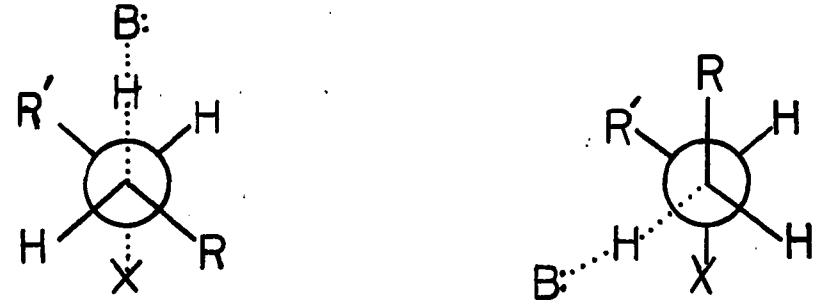
[a]No deuterium exchange yet thought to be a E_{1CB} cis elimination due to steric strain and beta proton acidity.

Table 9a. (Continued)

Compound	Base/solvent	Rel. rate, k_H/k_D and ρ	E_a (Kcal./mole)	$\Delta S^{\ddagger}$ (e.u.)	Ref.
$C_6H_5CH(OOCR)CHDC_6H_5$	t-BuO$^-$/t-BuOH				69
erythro and threo					
R = 2, 4, 6-triethylbenzene-trans eliminations is observed.					
R = methyl-cis elimination is observed and a base promoted cyclic mechanism proposed.					
$F_2HC-CCl_3$	$^-OCH_3/CH_3OH$	Eliminates 55 times faster than the rate of deuterium exchange. "Nearly E_{1CB}" transition state proposed			108

Table 9b. Beta elimination data of various acyclic systems

Compound	Base/solvent	%cis olefin	% trans olefin	Ref.
$C_3H_7CH_2\underset{\displaystyle X}{\underset{\vert}{C}}HC_4H_9$				
$-\overset{+}{N}(CH_3)_3$	$\underline{t}$-$BuO^-/\underline{t}$-BuOH	26	74	
	$CH_3CH_2O^-/CH_3CH_2OH$	74	26	
	CH_3O^-/CH_3OH	81	19	
$-\overset{+}{S}(CH_3)_2$	$\underline{t}$-$BuO^-/\underline{t}$-BuOH	9	91	
	$CH_3CH_2O^-/CH_3CH_2OH$	64	36	40



E_2 "central" transition state

E_2 "nearly E_{1CB}" transition state

Figure 3. Most stable rotomers of the transition states of 6-substituted nonane. X group is sterically much larger than the alkyl R groups (X >>>> R=R'>H)

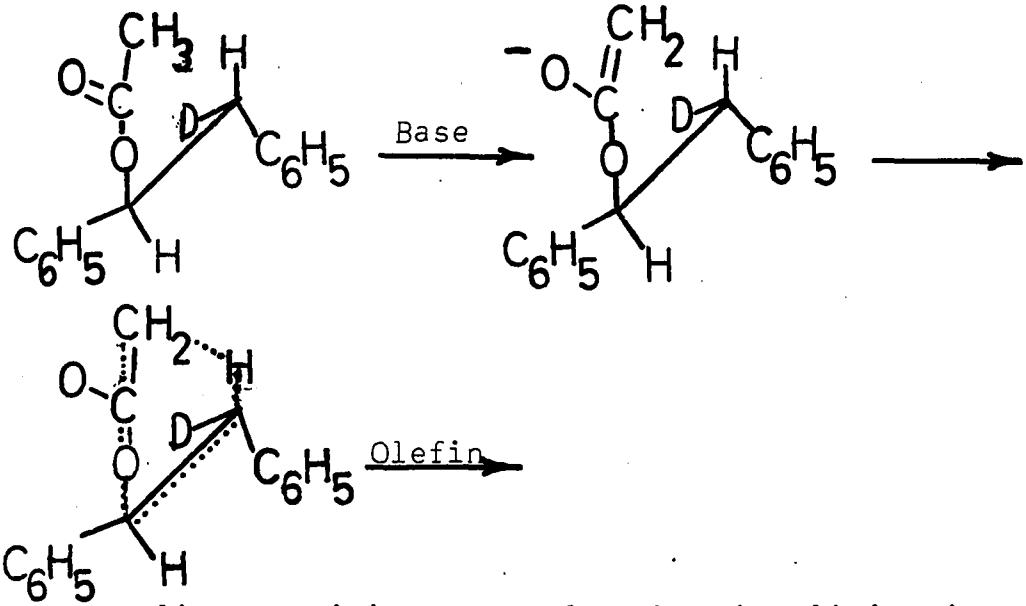


Figure 4. Cyclic transition state for the cis elimination of erythro-1, 2-diphenyl-2-deuteroethyl acetate

Curtin (69) found that the acetate esters of erythro and threo-1, 2-diphenyl-2-deuteroethanol underwent base-catalysed cis elimination. The triethylbenzoate esters did not undergo cis elimination under identical conditions. A cyclic mechanism (Figure 4) was proposed after a primary anion is formed.

The author suggests another cyclic mechanism in which the triethylbenzoate is not eliminated in a cis manner due to steric hindrance of the attack of base on the backside of the carbonyl (Figure 5).

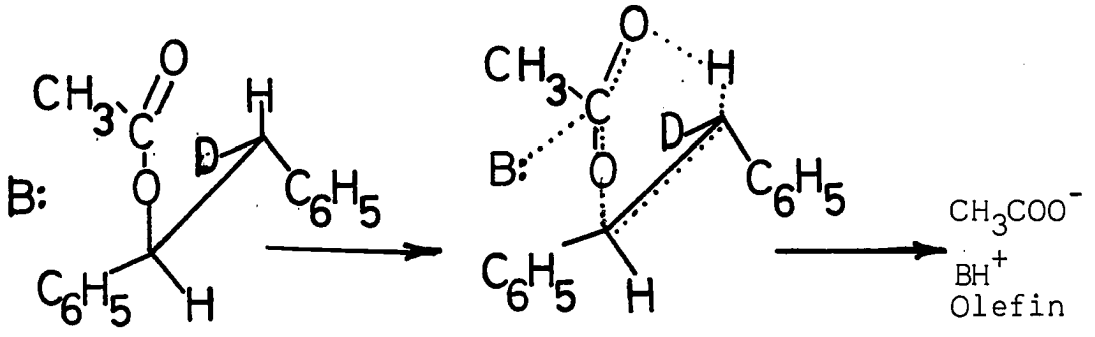


Figure 5. Alternate cyclic mechanism for the cis elimination of erythro-1, 2-diphenyl-2-deuteroethyl acetate

In all three types of E_2 mechanisms, there is evidence that the leaving group Table 10 plays an important role in the stereochemistry of the reaction. A great deal of attention has been devoted to characterizing leaving groups because much of the mechanistic evidence is derived from their relative ability as leaving groups. The p-toluenesulfonate moiety which may be the most common leaving group cannot be

assigned any relative position in the order of increasing leaving group ability. Bishop (6) proposed that the more C-oTos bond breaking in the transition state the better the p-toluenesulfonate group became as a leaving group. The partial charge on the oxygen is stabilized by resonance and an increase in that partial charge means a more stable partial anionic leaving group. In addition to this hypothesis, it is possible that p-toluenesulfonate group acts in a cyclic transition state to aid the removal of the beta hydrogen atom This is an extension of Skell's (8) "nearly E_1" cyclic transition state to all of the E_2 mechanistic pathways analogous to Curtin's (69) system.

Table 10. Relative rates of E_2 elimination reactions involving p-toluenesulfonate and halides as leaving groups

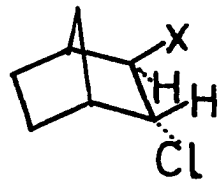
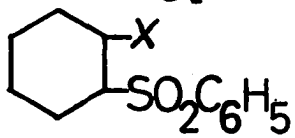
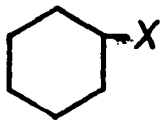
Compound	Type of Elimination	Base/solvent	Rate ratio k_F	k_{Cl}	k_{oTos}	k_{Br}	k_I	Ref.
	cis	Pentoxide/pentanol	--	1	6×10^5	--	--	104
	cis	OH^-/50% aq. dioxane	--	1	1.3	4	--	90
	trans		--	1	--	4	--	91
	cis	OH^-/80% ethanol	--	1	0.8	--	--	
	trans	OH^-/80% ethanol	--	180	1	--	--	109
t-Amyl-X	trans	t-BuO^-/t-BuOH	--	1	--	60	400	
$C_6H_5CH_2CH_2$-X	trans	$CH_3CH_2O^-$/ethanol	1	70	400	4,300	28,000	20,21 112
		t-BuO^-/t-BuOH	--	1	6	25	130	
		$CH_3CH_2O^-$/t-BuOH	--	--	1	5.6	27	
$(CH_3)_2CHCH_2$-X			--	--	4	3	--	113
General Sn_1		ethanol	--	--	20	1	2	112

Table 10. (Continued)

Compound	Type of Elimination	Base/solvent	Rate ratio k_F	k_{Cl}	k_{oTos}	k_{Br}	k_I	Ref.
General Sn_2	1° carbon		--	--	4	6	--	112
	2° carbon	acetone	--	--	4	3	--	56
XCH = CHX	cis	CH_3O^-/CH_3OH	--	1	--	8	285	
	trans		--	1	--	1,300	110,000	

RESULTS AND DISCUSSION

In most bimolecular elimination reactions (E_2), in systems $H\text{-}C_\beta\text{-}C_\alpha\text{-}X$, the attacking base and the leaving group are situated trans or anti to each other in the transition state (Figure 6).

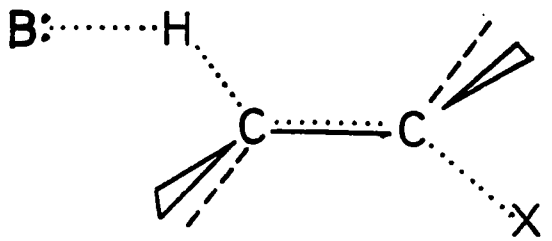


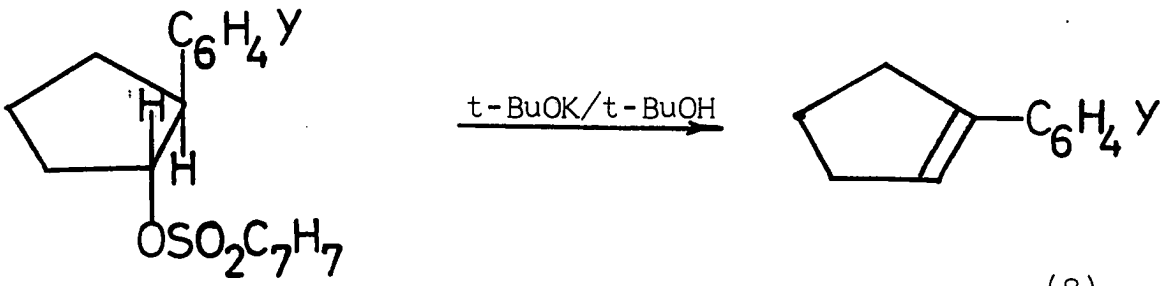
Figure 6. Transition state of trans E_2 elimination

However, there are cases of base promoted elimination reactions in which the antiperiplanar transition state is not the preferential conformation. Due either to the presence of an electron-withdrawing group activating the beta proton or to the fact that the molecule is not able to assume an anticoplanar transition state, cis elimination occurs. There is evidence that these reactions may involve the E_{1CB} or a carbanion mechanism in certain cases although the E_2 "nearly E_{1CB}" transition state has not always been excluded.

Cis eliminations can be placed into two kinetic categories. Elimination is very difficult in Cristol's (60-62) classic case of β-hexachlorobenzene in which the chlorine atoms are all trans to one another making trans elimination of hydrogen chloride impossible. In this case and in the trans-norbornyl

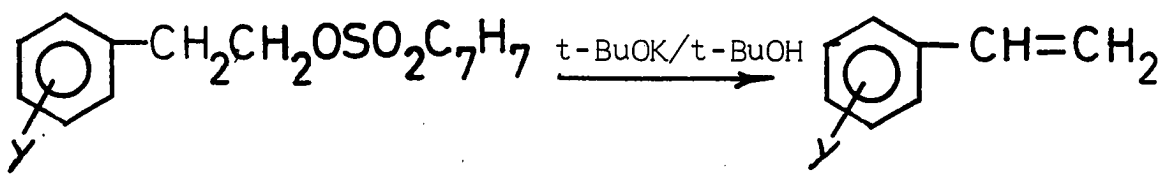
dichloride (104), trans-11, 12-dichloro-9, 10-dehydro-9, 10-ethanoanthracene (105, 106) and trans-dichloroacenaphthene systems (107) the forced cis elimination is kinetically very slow compared to the rate of elimination of β phenylethyl compounds at the same temperature. The rate of cis eliminations in these and similar systems increase approximately 10^{10} times when the β-proton is activated by β-sulfonyl derivatives. Cristol (105) Bordwell (87, 88), and Goering (91), using systems in which an anticoplanar transition state was unattainable and/or the β-proton acidified by the powerful electron withdrawing sulfonyl group on the β carbon atom, suggested that the cis elimination proceeded by a carbanion intermediate. Indeed, these activated, fast cis eliminations would proceed even when trans eliminations was structurally possible. The "detosylation" of trans-2-p-tolylsulfonyl-cyclopentyl p-toluenesulfonate yields 1-p-tolylsulfonyl cyclopentene with the double bond adjacent to the sulfone group rather than 3-p-tolylsulfonylcyclopentene, the product expected from trans elimination.

In contrast to the previous cis eliminations, DePuy, Thurn and Morris (38) reported that a rapid beta elimination of trans-2-arylcyclopentyl p-toluenesulfonates did not appear to react via the E_{1CB} mechanism. These compounds were reported to react readily with potassium t-butoxide-t-butanol solution giving clearly second order kinetics and 1-aryl-cyclopentene as the only product. The Hammett sigma-rho



(8)

correlation was applied to the system giving rho = +2.34. It was concluded that this cis elimination involved less carbanion character on the beta carbon atom than β-arylethyl p-toluenesulfonates under the same conditions. The β-arylethyl system is presumed to be a trans elimination and has a rho value of 3.39 under the same conditions.



(9)

The ratio of k trans E_2 to k cis E_2 was reported to be only 14 in the 2-arylcyclopentyl system. In an attempt to determine the effect on cis elimination of the dihedral angle between beta proton and the leaving group, k-trans/k-cis was determined to be greater than 10^4 for the 2-arylcydohexyl p-toluenesulfonates. The trans compound failed to react after 22 days in potassium-t-butoxide-t-butanol solution at 50°C.

This thesis presents the continuing investigation of the 2-arylcyclopentyl p-toluenesulfonate elimination reaction. The purpose was to clarify the nature of the reaction mechanism by confirming the cis stereochemistry of the reaction, conclusions drawn from Hammett rho values and k-trans/k-cis ratios of both cyclopentyl and cyclohexyl systems.

The beta elimination reaction of trans-2-arylcyclopentyl p-toluenesulfonate in potassium-t-butoxide-t-butanol solution was reported to give soley 1-arylcyclopentene as the product. This olefin can be produced by a cis elimination or a trans elimination of the substrate followed by a base catalyzed isomerization of 3-arylcyclopentene. The investigation of this system hoped to confirm the cis nature of the reaction by the following:

1. The study of the base-catalyzed equilibration of the 3 and 1-arylcyclopentenes.

2. Gas phase chromatographic analysis of the olefinic products.

3. The determination of the deuterium isotope effect.

Cis elimination is the only means of producing the 1-olefin if the 3-arylcyclopentene does not isomerize under elimination conditions. It is possible that small amounts of 3-arylcyclopentene are produced but escape detection by ultraviolet spectrophotometric analysis employed in the previous study. Gas phase chromotographic analysis of the products would be a valuable check for traces of the 3-olefin.

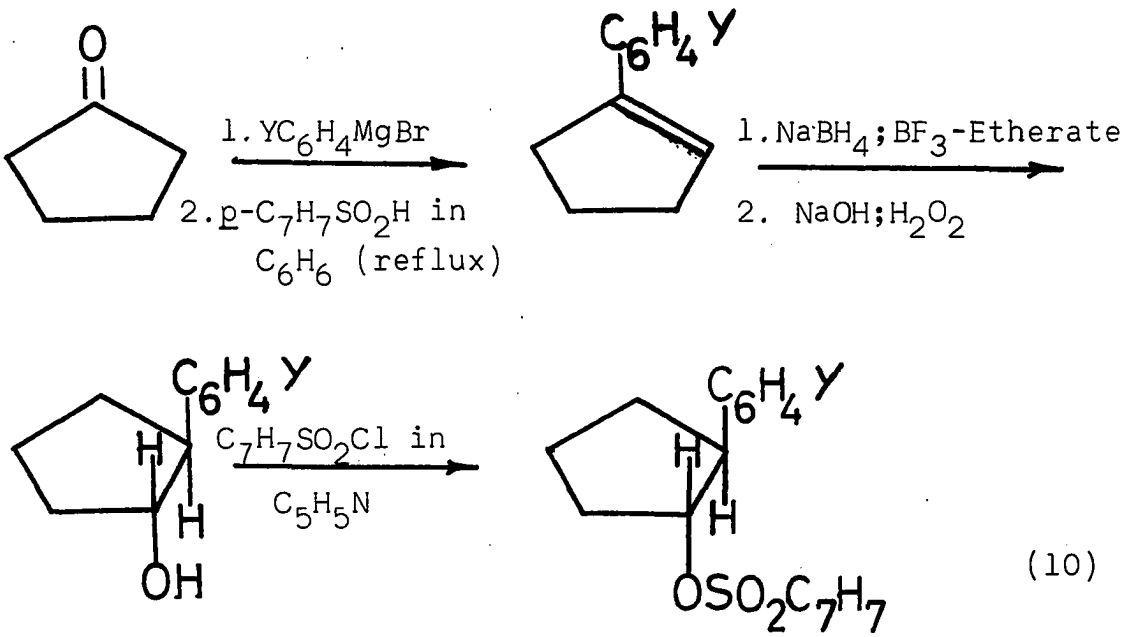
A deuterium isotope effect would confirm the loss of the cis hydrogen in the rate determining step. The magnitude of the deuterium effect is also a criteria for the allocation of the reaction's transition state within the E_2 spectrum of mechanisms. It may also be possible to exclude the E_{1CB} mechanism if a high k_H/k_D value is found because the beta proton is not considered to be acidic relative to the strong base, potassium t-butoxide-t-butanol in this elimination reaction. In the earlier study (38) the Hammett rho value for the cis elimination of trans-2-arylcyclopentyl p-toluenesulfonates in potassium t-butoxide-t-butanol solution was compared to the Hammett rho value for the trans elimination of β-arylethyl p-toluenesulfonates in the same base-solvent system. This comparison is considered very dangerous because of the two completely different substrates involved. The β-arylethyl compounds have a primary alpha carbon atom attached to the leaving group whereas the cyclopentyl system contains a secondary alpha carbon. The implications of this difference is not known for any system involving the p-toluenesulfonate moiety as the leaving group. Rho values for trans and cis eliminations of different systems may not have the same mechanistic implications because of the different electronic and steric requirements of the transition state. The electronic effect and stereochemistry of a cyclic compound contrasts that of an acyclic system. It is proposed that a more valid rho-value comparison would be the cis and

trans elimination reactions involving the cis and trans-2-arylcyclopentyl p-toluenesulfonates. The values obtained in such an investigation should help clarify the amount of carbanion character of these beta elimination reactions. The relative amount of beta carbon carbanionic character will be determined by the similarity or diversity of the rho values.

An examination of the cis elimination of trans-2-arylcyclohexyl p-toluenesulfonate in order to depict the transition state would aid in elucidating the effect of the dihedral angle on the rate of E_2 reactions. It is necessary to find conditions under which the cis elimination can be established and investigated. Deuterium isotope effect and Hammett sigma-rho correlation would be determined if cis elimination of the cyclohexyl compounds is feasible.

The synthesis of trans-2-arylcyclopentyl p-toluenesulfonates was realized by reacting an aryl Grignard reagent with cyclopentanone followed by acid catalyzed dehydration of the tertiary alcohol to the 1-arylcyclopentene. Hydroboration of this olefin gave good yields of the trans-2-arylcyclopentanols which were easily transformed into the corresponding sulfonates by the action of p-toluenesulfonyl chloride in pyridine solution.

The reexamination of the beta elimination reaction of trans-2-arylcyclopentyl p-toluenesulfonates in potassium t-butoxide-t-butanol was begun by studying the second order kinetics by acidimetry. It was immediately noticed that the



(10)

rate constants determined were more than two times the rate constants reported by DePuy, Thurn and Morris (38) (Table 11). An investigation into the cause of the increase in the rate constants showed that the rates were not reproducible from one base solution to another. This erratic behavior of second order rate constants in potassium t-butoxide-t-butanol solution is not without precedent. DePuy and Bishop (20) reported rates of β-phenylethyl bromide and p-toluene-sulfonate which were 10 to 15 per cent faster than those previously reported by Saunders (73). Bishop (6) concluded that the purity of the t-butanol was the reason for the increase in rates. He further stated that any further purification than two distillations from sodium were not

Table 11. Rate constants for the reaction of trans-2-arylcyclopentyl p-toluenesulfonates with potassium t-butoxide-t-butanol solution

Y	k x 10^4 at 46.8°C.[a] ($l\ mole^{-1}\ sec.^{-1}$)	k x 10^4 at 50°C.[b] ($l\ mole^{-1}\ sec.^{-1}$)
p-CH_3	0.5	1.15
H	1.3	3.09
p-Cl	4.8	13.6
m-Cl	10.3	35.8

[a]Rates reported by DePuy et al. (38).

[b]Rates from present work corrected for 1-arylcyclopentene concentration.

necessary. Upon studying Bishop's* results of β-phenylethyl p-toluenesulfonate with potassium t-butoxide-t-butanol it was noticed that the range of rate constants was large compared with experimental error (Table 12). Since repeated kinetic experiments did not give a reliable rate constant value for the elimination of 2-phenylcyclopentyl p-toluenesulfonate, the purity of the potassium t-butoxide-t-butanol solution was studied using the β-phenylethyl p-toluenesulfonate. The preliminary results in Table 12 show that the rate of the elimination reaction does not correspond to the purity of the t-butanol. The same base solution has given different rate

*C. A. Bishop, Chemistry department, Iowa State University of Science and Technology, Ames, Iowa. Rate data. Private communication to C. H. DePuy, Chemistry department, Iowa State University of Science and Technology, Ames, Iowa. (Circa 1959).

Table 12. The second order rates of the elimination reaction of β-phenylethyl p-toluenesulfonate in approximately 0.1M. potassium t-butoxide-t-butanol at 30°C.

Method	$k_2 \times 10^3$	t-BuOH Purification
2nd order	2.66	3-distillations
same solution one week later	2.29	from
2nd order	2.44	sodium
2nd order	2.29	3 x Na and 2xK
"	1.28	2 x Na and 3xK
"	2.06	2 x Na and 2xK
2nd order (13)	2.03	2 x Na[a]
psuedo 1st order[b]	2.00	4 x Na
psuedo 1st order[b]	2.16[c]	4 x Na
2nd order	1.84[c]	2 x Na
"	2.03[c]	"
"	2.03[c]	"
"	2.20[c]	"

[a]Average of 4 kinetic determinations.

[b]Base approximately 0.3M.

[c]C. A. Bishop, Chemistry department, Iowa State University of Science and Technology, Ames, Iowa. Rate data. Private communication to C. H. DePuy, Chemistry department, Iowa State University of Science and Technology, Ames, Iowa. (Circa 1959).

contents at different times. The rates of the elimination of the β-phenylethyl p-toluenesulfonate ranged from Bishop's reported value to more than a 25 per cent increase on that value. No constant value could be obtained. An attempt was made to standardize the potassium t-butoxide-t-butanol solution by comparing other rates of elimination reactions with the rate for β-phenylethyl toluenesulfonate in the same base-

solvent solution. This method of standardization of base solutions proved to be unsuccessful when applied to the elimination of trans-2-arylcyclopentyl p-toluenesulfonates. The rate constants of the cis elimination of the cyclopentyl compound would vary a great deal more than the rate constants of the β-phenylethyl p-toluenesulfonate with different base solutions. This rate comparison found fair success with the attempted elimination of trans-2-arylcyclohexyl p-toluenesulfonates but side reactions occurring in this reaction are reason to suggest that the standardization method is not acceptable.

An attempt was made to duplicate the previously reported results by adding impurities to the fresh potassium t-butoxide-t-butanol solutions. The experiments showed that the purity of the t-butanol could only be a small part of the problem. An equivalent amount of water was added to the potassium t-butoxide-t-butanol solution and the effect was only to lower the rate to the worst "pure" base solution measured in the current series (Table 13) but did not decrease the rate by a factor of three which would equal the previously published rate data for the elimination of trans-2-arylcyclopentyl p toluenesulfonates. Carbon dioxide was also introduced into the base solution as a possible contaminate but this only effected the titration end point observation which was not

Table 13. The second order rates of the elimination reaction of cis and trans-substituted (Y) 2-arylcyclopentyl p-toluenesulfonates in approximately 0.1M. base followed titrametrically

Y	Base/solvent	T (°C.)	$k_2 \times 10^4$ (l mole^{-1} sec.$^{-1}$)	1-Phenylcyclo-pentene (yield %)
trans H	t-BuO$^-$/t-BuOH	50	2.92	94.5 G.P.C.[a]
"	"	50	2.3	--
"	"	50	3.79	100 U.V.[b,c]
"	OH$^-$/t-BuOH	50	2.35	--
"	t-BuO$^-$/t-BuOH	30	.539	87.7 G.P.C.
"	"	30	.561	100 U.V.
"	"	70	17.5	76.9-88.8 G.P.C.[d]
Deuterium in 2-position	"	50	.788	70 G.P.C
"	"	50	.792	--
trans m-Cl	t-BuO$^-$/t-BuOH	50	35.8	--
"	EtO$^-$/t-BuOH	50	18.4	--
"	EtO$^-$/EtOH	50	.621	--
trans p-Cl	t-BuO/t-BuOH	50	13.9	--
"	"	50	13.4	--
trans p-CH_3	"	50	1.41	81.8 G.P.C.
cis H	"	50	32.2	100 G.P.C.
"	"	30	5.88	--

[a]G.P.C. ≡ Gas phase chromatography.

[b]U.V. ≡ Ultraviolet Spectrophotometry

> methods used to determine the relative yields of olefins

[c]Calculated % 1-olefin on the basis of E_a from the G.P.C. and rate data of the 70°C. kinetic runs is 81.5% (see Table 14).

[d]G.P.C. analysis was not consistent between an early and infinity point of the kinetic run. No isomerization observed.

the case with the earlier work.* The purity of the p-toluenesulfonates was checked by elemental analysis and by experimental infinity points of the kinetic determinations and both checked excellently with the calculated values. The standard hydrochloric acid was restandardized and no change in titer was observed.

Impure potassium was suggested as a factor involved in the erratic behavior of the rates of elimination. Two base solutions made from potassium freshly cut from the same stick led to different rates. Potassium could be purified by distillation (114) under argon and sealed in glass ampoules. The ampoules would be broken under the t-butanol. This procedure was not attempted.

It should be noted that all the second order elimination reactions were carried out in 0.1M. potassium t-butoxide-t-butanol solution which was protected from atmospheric carbon dioxide and water vapor. The solutions were used within one week of their preparation and therefore they were kept in round bottomed Pyrex glass flasks. The effect of glass was not determined at 50°C. Although the titer of the base did not change over any length of time, the glass may have had other effects.

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*G. F Morris, Chemistry department, Iowa State University of Science and Technology, Ames, Iowa. Rate data. Private communication. (196).

The states of aggregation of a potassium t-butoxide-t-butanol solution may be involved with the problem. At this time there is no evidence of the aggregation states in 0.1M. potassium t-butoxide-t-butanol solution. It is suggested that some idea concerning aggregation states could be obtained by varying the cation of the base from potassium to sodium to lithium. The state of aggregation would tend to increase as the cation changed from potassium to sodium to lithium.

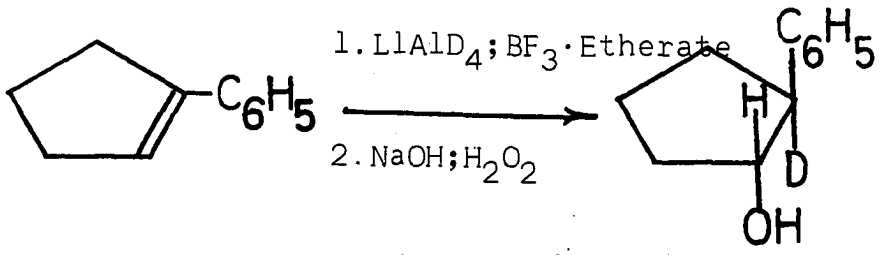
It was apparent that the problem concerning potassium t-butoxide-t-butanol in elimination reactions was not to be solved easily. Therefore, it was proposed to minimize the base's affects by running all the eliminations reactions with the same base solution. It was also suggested that the second order rates be determined by following psuedo first order kinetics by ultraviolet violet spectrophotometry of the conjugated olefin, 1-arylcyclopentene. The second order rates are obtained by dividing the psuedo first order rates by the base concentration. The means of measurement had many advantages over the previous titrimetric second order kinetic method. In psuedo first order kinetics any small changes in the base solution will be swamped out relative to the rate constants. Large changes in base solution are avoided by the use of only one solution for all the kinetic determinations. The analysis of the kinetic points of a determination by ultraviolet spectrophotometry eliminates the effect on the rate by the elimination reaction giving 3-arylcyclopentene

and solvolysis reaction producing non-olefinic compounds. Psuedo first order rates measured with a different base concentration might supply proof of the occurrence of solvolysis during the beta elimination reaction but this procedure is complicated by salt effects and previously described base effects.

Although there are many inconsistencies concerning rates determined in t-butanol, it must be noted that there is near perfect agreement between the second order rate constants obtained for the elimination of trans-2-arylcyclopentyl p-toluenesulfonates in approximately 0.1M potassium t-butoxide-t-butanol by the psuedo first order-ultraviolet spectrophotometric and the corrected second order-titrimetric measurements (tables 14 and 15).

The most important aspect of the present investigation of the beta elimination of trans-2-arylcyclopentyl-p-toluenesulfonates was to prove the cis nature of the reaction. This was accomplished by comparing the second order rate constants of 2-phenylcyclopentyl and 2-deutero-2-phenylcyclopentyl-p-toluenesulfonates in potassium t-butoxide-t-butanol at 50.0°C. Deuterium was introduced at the beta carbon atom by the deuteroboration of 1-phenylcyclopentene (Equation 11) and its position confirmed by nuclear magnetic spectroscopy.

The deuterium isotope effect definitely shows that the beta elimination reaction which gives the 1-phenylcyclopentene as the product must be cis in nature (Table 13). The deutero



(11)

compound reacts approximately five times slower than the undeuterated substance which can only be due to the base attack of the beta proton or deuteron in the rate determining step. The deuterium isotope effect is 5.6 ± 0.4 after the rate constants have been corrected for the trans elimination reaction forming 3-phenylcyclopentene. The second order rates of both 2-phenylcyclopentyl and 2-deutero-2-phenylcyclopentyl p-toluenesulfonates were measured by the titrimetric procedure. Identical reactions were simultaneously carried out to ten half-lives and prepared for gas chromatographic analysis of the products. The second order rate constant of the cis elimination was calculated by multiplying the over-all rate constant by the percentages of 1-phenylcyclopentene produced. Although inaccuracies exist in the olefin analysis, the reaction of 2-deutero-2-phenylcyclopentyl p-toluenesulfonate was reproduced in both kinetic and olefin analysis. The undeuterated compound could not be satisfactorily duplicated and an estimate of the cis elimination's second order rate constant was calculated from kinetic and olefin analysis at 30° and 70°C. The calculated value obtained agreed perfectly with the rate obtained by psuedo first order-ultraviolet

Table 14. The second order rates of the elimination reaction of trans-substituted-2-arylcyclopentyl p-toluenesulfonates corrected for olefin yield in approximately 0.1M. potassium t-butoxide-t-butanol solution

Y	T °C.	k_{E_2} (1-olefin) x 10^4 (l. mole^{-1} sec.$^{-1}$)	k_{E_2} (3-olefin) x 10^4 (l. mole^{-1} sec.$^{-1}$)
H	30	0.473	.066
H	50	3.09 calculated [a]	.70[a]
H	50	.553	.24
(deuterium in 2-position)			
H	70	15.5	2.0
pCH$_3$	50	1.15	.27
pCl	50	13.6[b]	
mCl	50	35.8[b]	

[a]Calculated using E_a from 30 and 70°C. rate data and the best rate of the hydrogen compound at 50°C.

[b]1-Olefin was assumed to be 100%.

spectrophotometric means (Tables 13, 14 and 15). It is without a doubt that the deuterium isotope is real and even with liberal estimates of error involved the effect is numerically between 5 and 6. This value of k_H/k_D is too large for an E_{1CB} mechanism to operate in this system. The beta proton is not acidic relative to the strong base t-butoxide. The expected k_H/k_D is small for an E_{1CB} transition state in this system which would be related to the "carbanion-like E_{1CB}" transition-state in Figure 2.

The cis nature of the elimination reaction was confirmed

Table 15 The psuedo first order rates of the elimination reaction of cis and trans substituted (Y) 2-arylcyclopentyl p-toluenesulfonates in approximately 0.1M. potassium t-butoxide-t-butanol solution (ultraviolet spectrometry)

Y	T (°C.)	$k_{E_2} \times 10^4$ (l. $mole^{-1} sec.^{-1}$)	1-Phenylcyclopentene yield (%)[a]
trans H	50	3.0	100
H	30.3	.483	95
m-Cl	50	35.4	100
p-Cl	50	13.6	100
p-CH_3	50	1.13	96
cis H	50	29.1[b]	100
H	30.3	5 95	100
m-Cl	50	93 6[b]	100
p-Cl	50	50.4[b]	100
p-CH_3	50	13.4[b]	100
β-phenylethyl p-toluenesulfonate	30.3	20.0[b]	100% styrene (20)

[a]The beta elimination of the corresponding cis compounds were assumed to go 100% to the 1-olefin.

[b]Average of duplicate runs.

by the fact that pure 3-phenylcyclopentene did not undergo any base catalyzed isomerization to the 1-phenylcyclopentene in approximately 0.1M. potassium t-butoxide-t-butanol solution between 30° and 70°C.

The Hammett equation (42, 115) (Equation 12) states that the rates (k) of the meta or para substituted benzene compound are related to the rate (k_o) of the unsubstituted compound by a reaction parameter ρ and a substituent constant σ. The

reaction parameter ρ is a measure of the difference in electron

$$\log \frac{k}{k_o} = \rho\sigma \qquad (12)$$

density at the phenyl-bearing carbon atom between the ground state and the transition state. In beta elimination reactions ρ measures the amount of negative charge on the beta carbon atom in the transition state. The ρ-values in Table 16 were calculated by the method of least squares from a log k/k_o versus σ plot.

The ρ-values for the cis elimination of trans-2-arylcyclopentyl-p-toluenesulfonates are +2.69, +2.76 and +2.77. The average value seems experimentally sound since three separate determinations give a constant value. DePuy et al. (38) previously reported a rho value of 2.34 which was low due to the unsuspected inconsistencies in rate constants when potassium t-butoxide-t-butanol was used as the base-solvent system. Mechanistically, the transition state does have considerable carbanion character but is definitely not an example of an E_{1CB} mechanism. Since the ρ value increases with decreasing temperature, the value obtained for the cis elimination is almost the same as the value (3.39) for the trans elimination of β-phenylethyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 30°C. (20). More intructive is the comparison of the ρ-value for cis elimination with the ρ-value for the trans elimination of the 2-arylcyclopentyl p-toluenesulfonates. In the trans elimination, which is

Table 16. Hammett correlations of rates, enthalpies and entropies of activation for the beta elimination of cis and trans-2-arylcyclopentyl p-toluenesulfonates

Compound	Base	Solvent	ρ (at 50°C.)	E_a (Kcal./mole)	$\Delta S^{\ddagger a}$ (e.u.)
trans[b]	0.1N t-BuO$^-$	t-BuOH	2.76±0.04	18.4	-18.1
trans[c]	0.1N t-BuO$^-$	t-BuOH	2.77±0.03	18.4	-17.5
trans[d]	0.3N t-BuO$^-$	t-BuOH	2.69±0.05	17.0	-21.5
cis[e]	0.1N t-BuO$^-$	t-BuOH	1.48±0.09	15.7	-21.7
cis[f]	0.2N EtO$^-$	EtOH	0.99±0.06	--	--
cis[g]	0.1N t-BuO$^-$	t-BuOH	--	16.5	-18.9

[a] $\Delta S^{\ddagger}$ was calculated from the following equation using the rate at 50°C.:

$$\Delta S^{\ddagger} = R[2.303 \log k_{50°C.} + \frac{E_a}{RT} - 2.303 \log (\frac{KT}{h})]$$

[b] Table 14. (Second order elimination reaction)

[c] Table 15. (Psuedo first order elimination reaction)

[d] Table 18. (" " " " ")

[e] Table 15. (" " " " ")

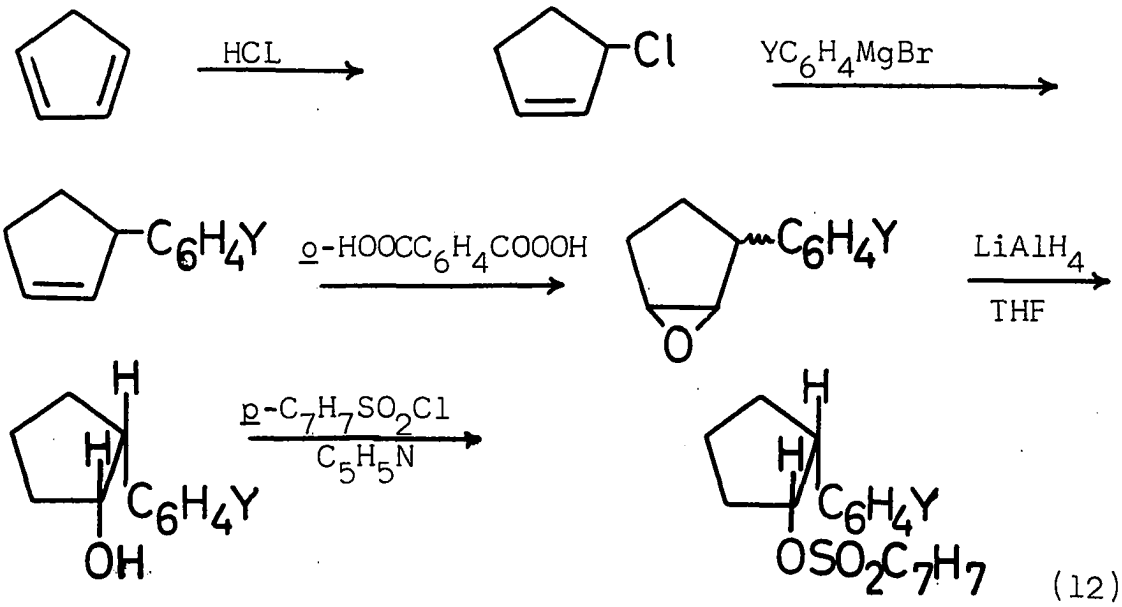
[f] Table 20. (" " " " ")

[g] Table 13. (Second order elimination reaction)

kinetically favored, the ρ-value (+1.48) is approximately one-half of the ρ value for cis elimination indicating that the cis elimination has more carbanion character in the transition state than the trans elimination. In order to place either reaction in the spectrum of E_2 transition states the deuterium isotope effect of the cis elimination was studied.

The ρ-value and deuterium isotope effect places the cis elimination's transition state near the "central" E_2 transition state. The trans elimination is between the "central" and "nearly E_1" transition states which gives the interesting conclusion that the cis elimination has a more synchronous E_2 transition state than the trans elimination.

The synthesis of cis-2-arylcyclopentyl p-toluenesulfonates was accomplished by use of the following reactions: Cyclopentadiene was hydrochlorinated and the resulting 3-chlorocyclopentene reacted with an aryl Grignard reagent to produce 3-arylcyclopentene. Epoxide(s) were synthesized from the olefin by the action of monoperoxyphthalic acid. The epoxides were reduced with lithium aluminum hydride in tetrahydrofuran producing the cis alcohol which was converted into the p-toluenesulfonate by the action of p-toluenesulfonyl chloride in pyridine.



(12)

As stated previously, trans elimination is kinetically favored over cis elimination. The trans-2-arylcyclopentyl p-toluenesulfonates rate ratio k trans E_2/k cis E_2 is 9.4 for the 2-phenyl and the rate ratio decreases to 2.6 for the meta-chloroaryl compounds because of the different ρ values. It was of interest to note that the rates of cis and trans elimination would become identical at a σ-value of 0.7 which corresponds approximately to the σ value of the nitro group.

Westheimer (33) presented the modern interpretation of the deuterium isotope effect recently. The elimination mechanism of trans-2-arylcyclopentyl p-toluenesulfonates is based partially on a k_H/k_D value. The side of the "central" transition state this value lies is a point of conjecture. For example, a k_H/k_D value of 5.6 may mean one of two things. Either the beta proton is not quite 50 per cent broken or it is just more than 50 per cent broken. It would be of interest to measure k_H/k_D values for the aryl compounds used in the Hammett correlation. As the meta or para substituent becomes more electron withdrawing, the transition state will favor the "nearly E_{1CB}" type of mechanism. It is suggested that the deuterium isotope effect be measured for the p-CH_3 and a m-Cl or m-CF_3 substituent in the trans-2-arylcyclopentyl p-toluenesulfonate system. If the k_H/k_D value decreases from the p-CH_3 compound to the m-Cl or m-CF_3 compound, then the transition state is on the "nearly E_{1CB}" side of the "central" mechanism. If an opposite result occurred, then transition

state would be on the "nearly E_1" side of a "central" mechanism.

The beta elimination of trans-2-arylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution proceeds in a concerted cis manner. The transition state of the cis elimination contains more carbanion character than the trans elimination's activated complex of the same carbon system. By a general comparison with the trans elimination of β-phenylethyl p-toluenesulfonate under similar reaction conditions it is presumed that the cis elimination proceeds via a "central" E_2 transition state. The present data limits the ability to depict more precisely the transition state or to state on which side of the "central" position the cis elimination's activated complex lies. Yet, it is conclusive that this case is the first example of a rapid concerted cis elimination.

Solvent effects in beta elimination chemistry were treated by Bunnett (2) in a general way as they effected the spectrum of E_2 transition states. A solvent with a high dielectric constant favors charge separation or the "nearly E_1" mechanism. It is not clear how the solvent changes effect other transition state criteria, such as Hammett rho-values.

Three conclusions were drawn from the present investigations on the solvent effects of elimination reactions.

1. The solvent has different effects on cis and trans eliminations of 2-arylcyclopentyl-p-toluenesulfonates.

2. Potassium ethoxide-t-butanol probably exists as an equilibrium of the bases.

3. Solvent changes are directly connected with transition state changes due to differences in base strengths and solvation of the leaving group in beta elimination reactions.

The rate of trans elimination of cis-2-arylcyclopentyl p-toluenesulfonates is nearly the same in potassium t-butoxide -t-butanol solution as in sodium ethoxide-ethanol solution. The rate ratio of $\frac{\text{k-butoxide}}{\text{k-ethoxide}}$ is only slightly greater than one for the unsubstituted, para and meta chloro derivatives. The ratio is less than one for the para methyl compound due to a difference in the Hammett rho values between the two base-solvent systems. The trans elimination of cis-2-phenylcyclopentyl p-toluenesulfonate shows almost no rate change corresponding to a change in the base-solvent system from potassium t-butoxide-t-butanol to sodium ethoxide-ethanol. Assuming there is no effect on the reaction by the cation of the base, the lack of rate change can be explained by the decrease in base strength or beta proton removing power being equivalent to the increase in solvation of the leaving group as the system changes from potassium t-butoxide-t-butanol to sodium ethoxide-ethanol. There is no data available concerning the effect of cations on the rate or mechanism of beta elimination reactions.

The solvent ratio of the corresponding cis elimination was more difficult to determine because the trans isomers

solvolyzed readily in ethanol solution. Solvolysis of cis-2-(4-methylphenyl) and trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonates was shown in sodium ethoxide-ethanol solution by the low yields of 1-arylcyclopentene found at the infinity point. In case of the cis compound very little solvolysis occurred and the error caused by the E_1 reaction producing 1-arylcyclopentene, as measured by ultraviolet spectrophotometry, is very small. The error was corrected by using a more concentrated sodium ethoxide-ethanol solution in the elimination reaction. The stronger base solution increased the 1-olefin yield by 8 per cent and decreased the second order rate constant by 10 per cent. All other cis compounds did not show a significant amount of solvolysis relative to the rate of elimination.

In contrast the trans-2-(3-chlorophneyl) cyclopentyl p-toluenesulfonate in 0.2M. sodium ethoxide-ethanol gave only 64 per cent of the 1-arylcyclopentene and a decreasing rate constant. It was estimated that ethanolysis was occurring at approximately the same rate as the beta elimination. The beta elimination rate ratio of potassium t-butoxide-butanol to to sodium ethoxide-ethanol solution is greater than one hundred estimating that the second order rate constant listed (Table 17) is high due to the 1-arylcyclopentene produced by solvolysis. The titrimetric rate constant (Table 13) is twice that measured by psuedo first order conditions (Table 17). It seems certain that the $\frac{\text{k-butoxide}}{\text{k-ethoxide}}$ ratio for the cis

elimination is at least 75 times greater than the corresponding ratio of the trans elimination. It is reasonable to conclude that a change in base-solvent system would effect the rate of a "nearly E_{1CB}" E_2 mechanism more than the rate of a reaction having a "nearly E_1" transition state. The rate of a reaction with a transition state on the E_{1CB} side of the "central" mechanism would be greatly influenced by the relative strengths of bases used. The solvation effect is very small and it is only a factor when the leaving group is almost removed in the rate determining step. The "nearly E_1" transition state of a reaction would be favored by the increase in solvation but this effect may be partly or totally compensated by the decrease in base's ability to remove the beta hydrogen atom.

It is suggested that the cis elimination of trans-2-arylcyclopentyl p-toluenesulfonates proceeds through a rate determining step on the E_{1CB} side of the theoretical "central" transition state and therefore the rate of elimination was greatly reduced due to the decrease in base strength as the base solvent system was changed from potassium t-butoxide-t-butanol to sodium ethoxide-ethanol. The trans elimination, having a mechanism on the E_1 side of the "central" transition state, was not effected to any great extent b, a change in solvent because the change in base strength was compensated by the increased solvation of the leaving group. Further experimentation could show that the solvent ratio or effect

could be an important criteria for determining the reactions relative location in the spectrum of E_2 transition states.

In conjunction with the effort to determine the $\frac{\text{k-t-butoxide}}{\text{k-ethoxide}}$ ratio for the cis elimination of trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate, a series of reactions were carried out in potassium t-butoxide-t-butanol solution with increasing amounts of absolute ethanol. It was hoped that the experimental rate data would produce a curve which could be extrapolated to 100 per cent ethanol. The second order rate constants decreased rapidly with increasing weight per cent of absolute ethanol added to the base-solvent system (Table 17 and Figure 7). The curve is smooth with no discontinuity at the 1.94 weight per cent ethanol point where the moles of ethanol exactly equal the moles of potassium t-butoxide. The graph suggests that there exists a slow, gradual change in base strength as the per cent ethanol is increased. There is a greater effect with the first few weight per cent of added ethanol than with subsequent additions. The first 10 per cent lowers the rate by a factor of three which cannot be extrapolated to give a meaningful rate constant at 100 per cent ethanol. No solvolysis was observed in any of the mixed solvent-rate measurements.

It is suggested that a good value of the rate constant of the beta elimination reaction of trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate could be measured by using a

Table 17. The psuedo first order rates of the elimination reaction of trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in approximately 0.3M potassium t-butoxide-t-butanol solution with varying weight percentages of ethanol followed by ultraviolet spectrometry

Solvent (Wt. % ethanol)	T (°C.)	$k_{E_2} \times 10^4$ (l. mole^{-1}sec.$^{-1}$)	1-Phenylcyclopentene (yield (%))[a]
0	50	45.3	100
0.96[b]	50	37.9	100
1.94[b]	50	32.5	100
3.88[b]	50	26.0	100
9.80[b]	50	15.3	100
100[b]	50	0.398	64

[a]The beta elimination of the cis compounds in t-BuOK/t-BuOh solution were assumed to give 100% 1-olefin.

[b]Base-solvents became yellow at 50°C.

2M. solution of sodium ethoxide in ethanol at 50°C. The exclusion of oxygen from the concentrated base solution is necessary in order to eliminate condensation side reactions. If solvolysis occurs, the sodium ethoxide-ethanol solution can be diluted with t-butanol and the rates extrapolated to 100 per cent ethanol.

The Hammett rho-value was obtained for the trans elimination of cis-2-arylcyclopentyl p-toluenesulfonates in sodium ethoxide-ethanol solution. The ρ of +0.99 is two-thirds of the rho value for the same reaction in potassium t-butoxide-t-butanol solution (Table 16). This rho value-solvent comparison is analogous to Bishop's (6) study of the β-phenyl-

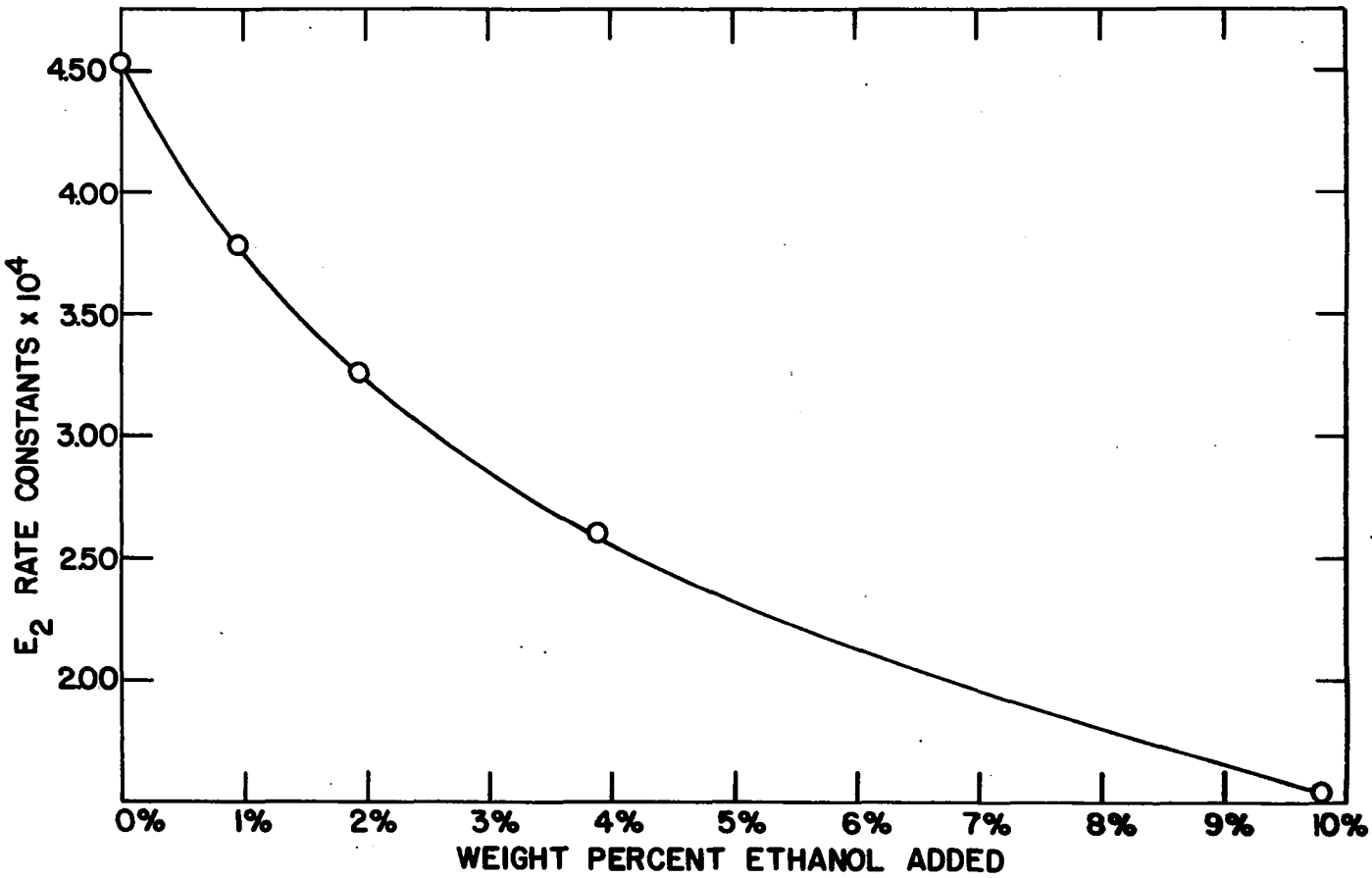


Figure 7. E_2 rates of trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in 0.3M. potassium t-butoxide-t-butanol solution with increasing weight percentages of ethanol

ethyl p-toluenesulfonate elimination reaction. The rho value determined in ethanol is also two-thirds of the rho value measured in t-butanol for the β-phenylethyl system. This interesting result, although a possible coincidence, supports interpretation by DePuy and Bishop (20) concerning the transition state proposed for the beta elimination of β-phenylethyl-p-toluenesulfonates. The solvent change from t-butanol to ethanol has shifted the transition state of the trans elimination more toward the "nearly E_1" mechanism. The solvent change encompasses an increase in the solvation of the leaving group and a decrease in the breaking of the beta proton bond due to a reduction in base strength. DePuy and Bishop (20) state that the base strength is the major factor involved in the decrease observed in the ρ-value for the elimination reaction involving β-phenylethyl p-toluenesulfonate when the solvent system is changed from t-butanol to ethanol. This was supported by data showing that the ρ-value decreased to nearly the value found in sodium ethoxide ethanol when the β-phenylethyl system was measured in potassium ethoxide-t-butanol solution.

The rates of the cis elimination of trans-2-arylcyclopentyl-p-toluenesulfonates in 0.1M. (Table 15) and 0.3M. (Table 18) potassium t-butoxide-t-butanol solutions show that solvolysis does not occur. In each case, the rate in the stronger base is approximately 1.4 times faster than the rate in the weaker base. This effect can be attributed to a salt effect, an increase in the ionic strength increasing the rate

of the elimination reaction. It is important to notice at this point that the rates of β-phenylethyl p-toluenesulfonates were also measured in these two base solutions at 30.3°C. and recorded in Tables 15 and 18. The apparent salt effect of the elimination reaction of β-phenylethyl p-toluenesulfonate was small (1.1) compared to the cis elimination involving the trans-2-arylcyclopentyl compounds. Table 19 shows the salt effect data.

All reactions involving ions are subject to salt effects. If a reaction requires separation of positive and negative charge during formation of the transition state, it will be favored by high ionic strengths. If charge is partially neutralized or dispersed during formation of the transition state, the reaction will generally proceed more rapidly in solutions of low ionic strength. If the increase of the second order rates with increase in base strength is a salt effect it may be interrupted mechanistically as the β-phenylethyl p-toluenesulfonate elimination being nearer the "central" E_2 transition state than the cis elimination of trans-2-arylcyclopentyl p-toluenesulfonate. To be sure, there is no data concerning the salt effect in E_2 eliminations reactions to aid in any interpretations of salt effect data. In this particular study the increase in rate due to the increase in base strength may be due to unknown composition of the potassium t-butoxide-t-butanol solutions already discussed in this thesis.

Table 18. The psuedo first order rates of the elimination reaction of trans-substituted (Y) 2-arylcyclopentyl ptoluenesulfonates in approximately 0.3M. potassium t-butoxide-t-butanol solution followed by ultraviolet spectroscopy

Y	T (°C.)	$k_{E_2} \times 10^4$ (l. $mole^{-1} sec.^{-1}$)	1-Phenylcyclopentene yield (%)[a]
H	50	4.23	95
H	30.3	.757	95
p-CH_3	50	1.63	85.5
m-Cl	50	45.3	100
β-phenylethyl p-toluenesulfonate	30.3	21.6	100 (20)

[a]The beta elimination of the cis compounds in t-BuOK/t-BuOH solution were assumed to give 100% 1-olefin.

Table 19. Apparent salt effect of cis elimination of 2-arylcyclopentyl p-toluenesulfonates

Compound	T (°C.)	Rate 0.3M. base / Rate 0.1M. base
H	50	1.32
H	30.3	1.57
p-CH_3	50	1.44
m-Cl	50	1.23
β-phenylethyl p-toluenesulfonate	30.3	1.08

Table 20. The psuedo first order rates of the elimination reaction of cis-substituted (Y) 2-arylcyclopentyl p-toluenesulfonates in approximately 0.2M. sodium ethoxide-ethanol solution followed by ultraviolet spectrometry

Y	T (°C.)	$k_{E_2} \times 10^4$ (l. $mole^{-1} sec.^{-1}$)	1-Phenylcyclopentene yield (%)[a]
H	50	24.2	95.5
p-CH_3	50	19.3	87
p-Cl	50	47.5	100
m-Cl	50	62.8	100
p-CH_3[b]	50	17.3	94.5

[a]The beta elimination of the cis compounds in t-BuOK/t-BuOH solution were assumed to give 100% 1-olefin.

[b]Base concentration approximately 0.5M.

There is lack of agreement between the per cent yields of 1-arylcyclopentene analyzed by gas phase chromatography and ultraviolet spectrophotometry Tables 13 and 15. In many cases shown in Table 15 the ultraviolet spectrophotometric analysis of the 1-olefin product is considerably higher than the amount found by gas chromatographic analysis. This inconsistency could be caused by isolation techniques for gas phase chromatographic samples and/or incorrect molar extinction coefficients used in the spectral method of analysis. The erratic behavior of potassium t-butoxide-t-butanol solution may also be a factor in the product analysis.

It is also noted that the percentage yields of 1-arylcyclopentenes in Tables 15 and 18 were less than one hundred

for the cis elimination of trans-2-arylcyclopentyl p-toluenesulfonates in 0.1M. potassium t-butoxide-t-butanol. When the same reactions were carried out in 0.3M. base the olefin product percentages were lower in each case. The remaining product must be the 3-arylcyclopentene because the increase in base strength did not reveal any evidence for the occurrence of solvolysis. The reason for the increase in 3-olefin production with increase in base concentration is not clear if, indeed, it is a real phenomena. It is suggested that in subsequent psuedo first order rate measurements the infinity point product analysis be checked by gas phase chromatography. More experimental data is needed before an explanation can be found for differences in 1-arylcyclopentene yields by the same or different methods of analysis.

The para-toluenesulfonate is a poorer leaving group than bromide in the beta elimination of β-phenylethyl compounds. The reverse is true in displacement and solvolysis reactions. Bishop (6) suggested that the leaving group ability of the p-toluenesulfonate group is strongly dependent on the amount of carbon-oxygen bond breaking in the transition state. The p-toluenesulfonate group was proposed to be a poor leaving group when little carbon-oxygen bond breaking exists in the transition state. Conversely, when carbon-oxygen bond breaking is extensive, the effect of resonance stabilization of the strong partial negative charge makes p-toluenesulfonate a good leaving group. Bishop further suggested that in carefully

controlled systems, the bromide-p-toluenesulfonate rate ratio might be useful as a measure of the extent of alpha carbon-leaving group bond breaking.

Bishop (6) also proposed another theory concerning p-toluenesulfonate-halogen rate ratios. He stated that in "nearly E_{1CB}" transition states, the p-toluenesulfonate apparently cannot relieve the negative charge on the beta carbon atom as well as the halides. This second statement about p-toluenesulfonate as a leaving group is a restatement of the conclusion concerning the bond breaking between the alpha carbon atom and the leaving group. It is suggested that the whole series of relative p-toluenesulfonate reactivities ranging from more reactive than bromide to less reactive than chloride depends on the position of the transition state in E_2 mechanism spectrum.

The bromide-p-toluenesulfonate rate ratio for the cis elimination of trans-2-arylcyclopentyl compounds should parallel the rate ratio for the β-phenylethyl system since the transition states of the reactions are thought to be very similar. The synthesis of 2-phenylcyclopentyl bromide was reported by Brown and Kühn (116, 117). They reported the following preparation of the bromide. 3-Phenylcyclopentene was heated in glacial acetic acid at 100°C. for 4 hours with anhydrous hydrogen bromide bubbled through the solution. The product was distilled and analyzed by making its Grignard reagent followed by carbonation and isolating the 2-phenyl-

cyclopentyl carboxylic acid. A 20 per cent yield of this acid was obtained.

In the present investigation, free radical hydrobromination of 1 and 3-phenylcyclopentenes failed to produce any bromides. The Brown and Kühn (116, 117) synthesis was repeated. The bromine containing products gave two distinct peaks upon gas phase chromotographic analysis although dehydrobromination took place on the carbowax G.P.C. column. Nuclear magnetic resonance analysis verified that the product obtained was a mixture. The product mixture was carefully distilled on a Nester gold plated spinning band distillation column and the fractions collected were monitored by gas phase chromatographic analysis. According to G.P.C. analysis the mixture was cleanly separated. The major component was again subjected to nuclear magnetic resonance analysis. The spectra was definitely clearer but there was no doubt that a mixture of compounds was present. Gas phase chromatographic analysis with many different types of columns, including a 100 meter Golay 20SE silicone oil capillary column and thin layer chromatography failed to separate the mixture.

Kinetic and product analysis of the beta elimination of the bromide mixture in potassium t-butoxide-t-butanol solution gave the only information concerning the problem. The kinetic results are summarized in Table 12. The initial rate of the bromide mixture was very fast and decreased with elapsed time rapidly until 10% of the reaction was complete.

The reactions at 30° and 50°C. gave good rate constants between 20% and 80% completion. Product analysis showed that the mixture of bromides consisted of cis and trans-3-phenylcyclopentyl bromides. The products at the infinity point were 4-phenylcyclopentene (70%) and 3-phenylcyclopentene (30%). No 1-phenylcyclopentene was detected. The 4-phenylcyclopentene was found to have the same retention time on UCON LB 550 X 4:1 on Reg. W Chromosorb at 70°C. as an authentic sample synthesized by Dr. Gene F. Morris. Although there was no indication in the rate data that one of the isomers reacted faster than the other, nuclear magnetic resonance spectra showed that one isomer or compound of the bromide mixture was removed preferentially by the beta elimination reaction and at 85% completion one pure compound remained. The stereochemistry of this isomer could not be determined.

The rate of the elimination of the mixture of cis and trans-3-phenylcyclopentyl bromide was equal to the rate of beta elimination of cyclopentyl bromide under identical reaction conditions. The implication is that the ring conformations must be the same for both elimination transition states. The phenyl group has very little effect upon the elimination reaction suggesting that the envelope conformation of the cyclopentyl ring has placed the phenyl group in a "equatorial" position away from the rest of the ring (Figure 8). In other words, no cis steric interactions between the bromide and phenyl moieties. The initial fast rate in the 30°C. kinetic

measurement could be the rate of elimination of cis and/or trans-2-phenylcyclopentyl bromides. This conclusion indicates that the minor bromide product removed by the spinning band distillation was the 20 per cent yield of the 2-phenylcyclopentyl bromide reported by Brown and Kühn (116, 117). A large scale preparation of the 2-phenylcyclopentyl bromide was not undertaken at this time but, it may be feasible.

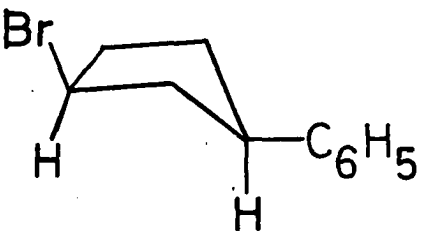


Figure 8. Envelope conformation of cis-3-phenylcyclopentyl bromide

The rate of elimination of the 3-phenylcyclopentyl bromide mixture at 50°C., which was calculated from the initial high rate at 30°C. assuming an enthalpy of activation of 16 Kcal./mole, is approximately equal to the rate of cis elimination of trans-2-phenylcyclopentyl p-toluenesulfonate. This preliminary results encourages further investigation into the synthesis and beta elimination kinetics of cis and trans 2-arylcyclopentyl bromides.

The enigma connected with the work on 3-substituted phenylcyclopentenes is the problem of isolating a pure isomer and identifying its stereochemistry It was thought that 3-

Table 21. Rates and activation parameters of the elimination reaction of cis and trans-3-phenylcyclopentyl bromide in potassium t-butoxide-t-butanol solution

Compound	σ (°C.)	$k_{E_2} \times 10^4$ (l. $mole^{-1} sec.^{-1}$)	E_a Kcal./mole	$\Delta S^{\ddagger a}$ (e.u.)
a mixture cis and trans of unknown composition	30	0.374	16.2	-25.4
	50	1.97	--	--

[a] $\Delta S^{\ddagger}$ calculated from equation given in Table 16 using the 50°C. rate constant.

phenylcyclopentanol compounds might be appliable to the problem. These alcohols were produced by the hydroboration of 3-phenylcyclopentene and the 2- and 3-phenylcyclopentanols were separated by a careful spinning band distillation.

The samples were analyzed by gas phase chromatography on the UCON LB 550X column. The 3-phenylcyclopentanol was produced in 35% yield which is somewhat different from Brown's (118) result of the hydroboration of 3-methylcyclopentene which gave 55% of the 3-alcohol. This product result suggests that the phenyl substituent influences the electronic condition of the hydroboration transition state. Raush* recently has shown that hydroboration of the 3-t-butylcyclopentene gives

*D. Raush, Chemistry department, Iowa State University of Science and Technology, Ames, Iowa. Private communication. (1963).

the same product ratios as 3-phenylcyclopentene which may indicate that the conformation of the cyclopentyl ring also effects the hydroboration transition state by steric factors. Further experimentation is necessary in order to discern the importance of the conformation of the cyclopentane ring on mechanism of various reactions.

The hydroboration of 3-phenylcyclopentene gave a 60:40 mixture* of trans to cis 3-phenylcyclopentanols in contrast to the 90:10 mixture of trans-2-phenylcyclopentanol to cis-2-phenylcyclopentanol. Nuclear magnetic resonance spectra indicated that the benzylic protons in 3-phenylcyclopentanols and their acetates were different but stereochemistry could not be assigned. The p-toluenesulfonates and 3, 5-dinitro benzoates were prepared and the isomers separated by fractional cystallization. No further work has been done on these compounds although the elimination rates of the p-toluenesulfonates and spectra of the pure alcohols isolated from the benzoates (119) are of great interest.

The epoxidation 4-phenylcyclopentene and reduction of the epoxide with lithium aluminum hydride to form the 3-phenylcyclopentanols would be another method of synthesizing these alcohols. This method was used by Henbest (120) to synthesize 3-methylcyclopentanol. It is hoped that future investigation in the 3-substituted cyclopentyl compounds will

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*Rough estimate of the isomers from nuclear magnetic resonance spectra, assuming the trans isomer is the more abundant compound.

help in the elucidation of the conformation of cyclopentene.

Some results concerning the bromide-p-toluenesulfonate rate ratio were not obtained in the 2-arylcyclopentyl system and it seemed necessary to investigate a related system. Cyclopentyl p-toluenesulfonate and halides were chosen for this study because the system contained the stereochemistry and the secondary alpha carbon atom of the five membered ring. These compounds, however, did not have an activated beta proton. The secondary alpha carbon atom and the unactivated beta protons should shift the transition state toward the "nearly E_1" end of the E_2 mechanistic spectrum. Therefore, it would be expected that the p-toluenesulfonate group would become a better leaving group relative to the bromide.

The experimental rate data in Table 22 shows the prediction to be true. The cyclopentyl p-toluenesulfonate eliminates twice as fast as the corresponding bromide in potassium t-butoxide-t-butanol solution at 50°C. The rates were reproducible. Analysis of the products by gas phase cromatography at the infinity point of the reactions showed that at least 98 per cent of the product was cyclopentene. Bishop's (6) hypothesis that the p-toluenesulfonate-bromide rate ratio is a qualitative guide for the placement of beta eliminations reactions in the E_2 spectrum of transition states was given substantial support by the reversal of the rate ratio from the β-phenylethyl to the cyclopentyl systems. β-phenylethyl p-toluenesulfonate was reported (20) to react 4.5 times slower

Table 22. Rates of the elimination reaction of cyclopentyl p-toluenesulfonate and halides in potassium t-butoxide-t-butanol at 50°C.

Compound	$k_{E_2} \times 10^4$ (l.mole^{-1}sec.$^{-1}$)	Rel. rate
I	10.6	400
oTos	3.86	150
Br	1.94	75
Cl	0.026[a]	1

[a]Elimination at 50°C. very slow and the rate recorded is only tentative.

than the bromide in potassium t-butoxide-t-butanol solution at 30°C.

The β-phenyl-α-methylethyl p-toluenesulfonate and halide system may show the consequence of a secondary alpha carbon atom in beta eliminations. The p-toluenesulfonate-bromide rate ratio is predicted to be more than 1/4.5 found for the β-phenylethyl compounds. Hammett rho correlations and possibly the deuterium isotope effect will determine the relative E_2 transition state. These criteria will test the validity of Bishop's hypothesis concerning the leaving group rate ratio.

As an interesting note to the previously discussed trans elimination reactions concerning trans-2-arylcyclopentyl p-toluenesulfonates to produce 3-arylcyclopentenes, the rate for elimination of cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C. does not correspond to

a predicted value calculated from the rate of 3-arylcyclopentene production. The rate of the trans beta elimination to give the 3-arylcyclopentene should be the same for all the 2-arylcyclopentyl p-toluenesulfonates at a given temperature. Two experimental rate constants for this reaction are in agreement although the calculated value for the unsubstituted compound does not agree (Table 14). Nevertheless, the rate of the base promoted elimination of cyclopentyl p-toluenesulfonate is at least 2.75 times faster than the rate of 3-arylcyclopentene production even after the former rate has been divided by two for the statistical factors involved. It is not clear at the present time why the trans elimination to produce the 3-olefin should be reduced by a factor of 2 to 3 by the addition of a phenyl group to the five membered ring. The conformation of the cyclopentyl ring may be responsible for the lack of agreement in these similar reactions.

In an attempt to depict the transition state of cis E_2 elimination reactions especially as it varies with dihedral angle between the leaving group and beta hydrogen atom, a study of the Hammett rho and the deuterium isotope effect of trans-2-arylcyclohexyl p-toluenesulfonates in potassium t-butoxide-t-butanol was undertaken. The p-toluenesulfonates of the trans cyclohexyl compounds were synthesized in a similar manner to the trans-2-arylcyclopentyl compounds.

DePuy et al. (38) stated that a plot of the rate of elimination versus the dihedral angle between the beta proton

and the leaving group will show maxima at both 0° and 180° and a minimum at 90°. It is generally believed that the trans or antiperiplanar elimination is favored over the cis or coplanar elimination for the spectrum of E_2 transition states. Cis elimination of a cyclopentyl system is coplanar (Figure 9) whereas cis elimination of a cyclohexyl system can only become coplanar under a very strained conformation. Figure 10 shows the most favorable conformation of the trans cyclohexyl compounds.

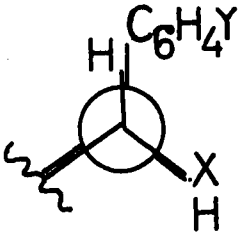

Figure 9. Trans cyclopentyl compound

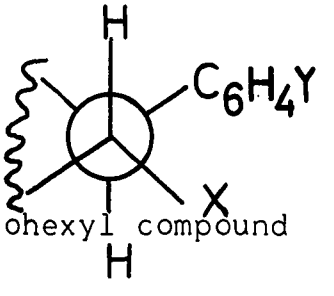

Figure 10. Trans cyclohexyl compound

The reaction of trans-2-phenylcyclohexyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 102°C. had a deuterium isotope effect of approximately unity. When the beta proton was activated by the electron withdrawing

effect of a meta-trifluoromethylphenyl group, the isotope effect increased to approximately two. This value appears to indicate that some cis elimination occurs in the reaction of trans-2-(3-trifluoromethylphenyl) cyclohexyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 102°C. It is not believed that the isotope effect for the solvolysis reaction accounts for the increase observed for the two compounds.

The rate ratio of the beta cis elimination of trans-2-(3-chlorophenyl) cyclopentyl and trans-2-(3-trifluoromethylphenyl) cyclohexyl p-toluenesulfonates was estimated. This cyclopentyl compound was chosen for the rate comparison because the Hammett sigma value is similar to that of the 3-trifluoromethylphenyl compound. The rate of the meta-chloro compound at 102°C. was calculated from the rate constant at 50°C. assuming an energy of activation of 16 Kcal. If it is assumed that the measured rate of the cyclohexyl compound represents only cis elimination, then the rate ratio is at least 500 favoring the cyclopentyl compound. The assumption, that the rate of trans-2-(3-trifluoromethylphenyl) cyclohexyl p-toluenesulfonate is all cis elimination, is probably not valid but a rate of one-half that value would be more reasonable. From the k_H/k_D values measured, it is estimated that the rho value of the cis elimination concerning the cyclohexyl p-toluenesulfonates might be greater than the rho value of the trans-cyclopentyl compounds. From these considerations,

it is estimated that the rate ratio of the cis elimination of trans-2-phenylcyclopentyl p-toluenesulfonate to trans-2-phenylcyclohexyl p-toluenesulfonate is 10^3.

The trans elimination of cis-2-phenylcyclohexyl p-toluenesulfonate is favored by a factor of 10^4 over its counterpart, the cis elimination, according to DePuy (38). The trans elimination is antiperiplanar whereas the cis is not coplanar. In contrast the cis-2-phenylcyclopentyl p-toluenesulfonate eliminates only 10 times faster than the trans isomer. In this case, the trans elimination cannot attain an antiperiplanar form in the cyclopentane ring, although this conformation can be approached in a slightly strained envelop configuration, whereas the cis elimination is easily coplanar.

The phenylnorbornyl system presents a unique case. The system is very rigid and does not allow any bending in the transition state without a considerable amount of energy being involved. The cis elimination in such a system is predicted to be faster than trans elimination because the trans configuration cannot approach an antiperiplanar conformation as was possible with the cyclopentane system. The cis elimination parallels the cyclopentane system and is coplanar. If the results are found as predicted it would indicate that the conformation of the cis-2-arylcyclopentyl p-toluenesulfonate is the evelope form with the dihedral angle approaching 180° in the transition state of a beta elimination.

The beta elimination reactions of trans-2-arylcyclohexyl p-toluenesulfonates were kinetically second order and they were followed by an acid titration of the excess base. Cis elimination was exceeding difficult in 0.1M. potassium t-butoxide-t-butanol solution at 102°C. Many problems beset the kinetic measurements and no meaningful beta elimination data was received. It was found that solvolysis occurred at a rate comparable to the rate of elimination.

3-Phenylcyclohexene isomerizes readily in 0.1M. potassium t-butoxide-t-butanol solution at 102°C. After 11 hours, the base catalyzed isomerization gave 40 per cent of 1-phenylcyclohexene as determined by ultraviolet spectrometry. The rate of isomerization is many times faster than the isomerization of 3-phenylcyclohexene to 1-phenylcyclohexene in potassium hydroxide-absolute ethanol solution at 100°C. reported by Weinstock and Bordwell (121).

The beta elimination which did occur in some of the trans-2-arylcyclohexyl compounds was not proven to be cis in nature. A small deuterium isotope effect was observed which might indicate a small amount of cis elimination. Product analysis was not attempted at this time because of the complication of the base catalyzed isomerization of olefins.

Experimental problems of these reactions were a great source of error. Potassium t-butoxide-t-butanol solution reacted with the Pyrex culture tubes used for reaction ampoules. A given amount of base was initially consumed by

the clean culture tubes at room temperature. At 102°C., a further reaction between the base and the glass gradually lowered the base's titer. Inconsistent rate results due to various solutions of potassium t-butoxide-t-butanol previously discussed were also obtained for this system.

The trans-2-(4-trifluoromethylphenyl) cyclohexyl p-toluenesulfonate under beta elimination conditions had an interesting side reaction. The rate of elimination increased almost exponentially with time and the reaction consumed more than 140 per cent of base necessary for calculated infinity point. In a preliminary investigation of this reaction it was noted that fluoride ion was a product. It was assumed that after a normal cis elimination reaction producing the 1-arylcyclohexene a second reaction occurred where t-butoxide attacked the 2-position on the 1-cyclohexene and substituted a fluoride ion in the p-trifluoromethyl group. The reaction of 1-(4-trifluoromethylphenyl) cyclohexene in 0.1M. potassium t-butoxide-t-butanol solution was followed kinetically by loss of base and production of fluoride ion both by titrimetric procedures. It was found that the loss of base was approximately twice as fast as the production of fluoride ion. No products of this reaction were isolated. The unique reaction may be of interest for future investigations.

It has been stated that an increase in electron withdrawing ability of a beta carbon substituent would favor the "nearly E_{1CB}" transition state. The reason for this shift

is probably a combination of two effects. First, an electron withdrawing substituent on the beta carbon atom would stabilize a carbanion intermediate or the partial negative charge of a "nearly E_{1CB}" transition state. Second, the beta hydrogen atom should become more acidic in a thermodynamic sense in the ground state. Therefore, it is more likely to be further removed from the beta carbon atom by the base in the transition state due to the increase in the electron withdrawing ability of a substituent on the β-carbon. In general, a cis elimination tends to have more carbanonic character associated with its transition state than the trans elimination of the same system. It is believed that the rate ratio of trans elimination to cis elimination decreases as the transition state of the cis elimination approaches the E_{1CB} mechanism. Bordwell (67, 68) using 1-nitro-2-phenyl-2-cyclohexyl acetate in piperidine, chloroform and ethanol concluded that both cis and trans isomers eliminate via an E_{1CB} mechanism. The cis elimination was four times faster than the trans elimination. The nitro group certainly makes the beta hydrogen more acidic and would stabilize a carbanion intermediate. Cristol (104) investigating norbornyl dichloride system found that the cis elimination was approximately 100 times faster than the trans elimination. He concluded at this time that the cis elimination proceeded by a carbanion intermediate whereas the trans elimination was a synchronous process. LeBel (103) has shown fairly conclusively that the norbornyl cis elimination system

has a "nearly E_{1CB}" transition state.

In relation to this hypothesis, the elimination of cis and trans-2-carbethoxycyclopentyl p-toluenesulfonate in sodium ethoxide-ethanol solution was kinetically determined. The system is analogous to the previously discussed 2-arylcyclopentyl p-toluenesulfonates except the carbethoxy group acidifies the beta proton more than the phenyl moiety.

It was felt that the sulfones used in all previous examples of fast cis elimination reactions could not be compared with the 2-arylcyclopentyl system because of the expanded electron octet in the sulfur atom of the sulfone. The sulfone according to Towns (122) can support a nonplanar carbanion although there is some question as to the interpretation of that data. Nevertheless, the present investigation was to measure the rates of cis and trans-2-carbethoxycyclopentyl-p-toluenesulfonates which do not contain a carbon-beta sulfur bond. This linkage may affect the mechanism as compared to the beta carbon-halide or p-toluenesulfonate bond. The comparison of this system with the 2-arylcyclopentyl compounds was more realistic due to the use of similar carbon skeleton.

The rate ratio of trans elimination to cis elimination for cis and trans-2-carbethoxycyclopentyl p-toluenesulfonates in sodium ethoxide-ethanol was 14. Both eliminations were very fast and the corresponding 1-olefin was produced quantitatively according to gas phase chromatographic analysis.

It was assumed that none of the 3-carbethoxycyclopentene was formed although no isomerization studies were carried out. The ratio of trans elimination to cis elimination increased approximately 10 fold from the arylcyclopentyl compounds to the carbethoxy compounds in the sodium ethoxide-ethanol base-solvent system. It is interesting to note that the trans-cis elimination rate ratio for the potassium t-butoxide-t-butanol base-solvent system of the arylcyclopentyl compounds is approximately that of the carbethoxy compounds. It is possible that the two different base-solvent-substrate systems have about the same E_2 transition state but there is no experimental proof of such a conclusion.

The replacement of the beta phenyl group with the carbethoxy substituent increased the rate of cis elimination approximately one million fold and about ten thousand fold for the trans elimination. This increase in rate is due in part to the increase in the thermodynamic acidity of the corresponding beta protons although no pK_a values are available.

The acidification of the beta hydrogen does seem to shift the reaction toward the "nearly E_{1CB}" side of the E_2 transition state spectrum. It does make cis eliminations more favorable relative to trans eliminations in the same system. But, the available data does not prove nor disprove the hypothesis that if the rate of cis elimination exceeds the rate of trans elimination, a E_{1CB} mechanism is involved.

Table 23. Rates of the elimination reaction of cis and trans-2-carbethoxycyclopentyl p-toluenesulfonate in sodium ethoxide-ethanol solution

Compound	T (°C.)	$k_{E_2} \times 10^2$ (l. $mole^{-1} sec.^{-1}$)	E_a Kcal./ mole	$\Delta S^{\ddagger a}$ (e.u.)
trans	0	3.40	15.7	-8.0
	-24.2	0.198	--	--
cis	-24.2	2.78	--	--

[a] $\Delta S^{\ddagger}$ was calculated from the following equation using the rate extrapolated to 50°C.

$$\Delta S^{\ddagger} = R[2.303 \log k_{50°C.} + \frac{E_a}{RT} - 2.303 \log (\frac{KT}{h})]$$

If the reaction does proceed via a carbanion intermediate the trans to cis elimination ratio of 14 is approximately the predicted value. The relief of steric interactions of cis-2-carbethoxycyclopentyl p-toluenesulfonate would increase the rate of the trans elimination relative to the cis elimination. The planar carbanion intermediate would remove the cis interactions. Any study which concerns cis and trans elimination must consider the effect of the dihedral angle beside the beta protons acidity and this makes any approach to this mechanistic problem exceedingly difficult.

The kinetic determinations involving the cis and trans-2-carbethoxycyclopentyl p-toluenesulfonates were very difficult because of the extreme rapidity of the elimination reaction at room temperature. The usual titrimetric procedure was not precise at the low temperature at which these reactions had

to be measured. Conductance (123-126) has been used frequently in organic chemistry to determine rates of solvolysis reactions. A very acceptable conductometric procedure was worked out to measure the rate of this bimolecular elimination reaction. The elimination reaction was allowed to take place in a conductance cell at the low temperature and resistance was measured at time intervals. An empirical calibration curve was used to convert resistance measurements to concentration terms. Second order kinetics were calculated in the usual manner. This method is more completely explained with sample calculations in the experimental portion of this thesis. Conductance was the only analytical tool available in this case of low temperature kinetics.

Deuterium exchange is the only positive criteria for the E_{1CB} mechanism. Using the above conductance procedure on trans-2-deutero-2-carbethoxycyclopentyl p-toluenesulfonate in sodium ethoxide-ethanol solution, small amounts of deuterium exchange would show up as an increase in rate as the reaction proceeds. It is believed that the conductance procedure could be refined to detect very small variances in the resistance-time plots. The synthesis of trans-2-deutero-2-carbethoxycyclopentanol was to be attempted by the deuteroboration of 1-carbethoxycyclopentene. If this synthesis could not be realized the exchange experiment could be measured using deutero-ethanol as solvent and the undeuterated p-toluenesulfonate.

Many papers concerning beta eliminations have activation parameters as collaborating evidence either for or against a given type of mechanism. It was noticed in the historical review and in the presented data (Tables 16 and 23) that there is absolutely no correlation of any kind with activation parameters and the mechanism of beta eliminations. The enthalpy and entropy of activation are approximately the same for the cis elimination of trans-2-carbethoxycyclopentyl p-toluenesulfonate and the trans elimination of β-phenylethyl and cis-2-arylcyclopentyl p-toluenesulfonate in sodium ethoxide-ethanol solution. These experimental parameters are subject to very large error terms (127). Interpretation given to entropy of activation is particularly dangerous unless the reactions are very carefully controlled. The present stage of knowledge concerning beta eliminations and the criteria of these eliminations such as ρ and k_H/k_D, does not allow any valid interpretation of activation parameters. At this time, these parameters show no promise in aiding the placement of beta elimination systems into the theoretical spectrum of transition states.

EXPERIMENTAL

Part I: Beta Elimination Studies of 2-Arylcyclopentyl p-Toluenesulfonates

Preparation and purification of material

Preparation of arylcyclopentyl compounds

3-Chlorocyclopentene 3-Chlorocyclopentene was prepared by bubbling anhydrous hydrogen chloride through cyclopentadiene. Freshly distilled cyclopentadiene (188 g.) was cooled to -15°C. Anhydrous hydrogen chloride was bubbled through the diene as fast as possible without loss of hydrogen chloride or raise in temperature. The addition was stopped as soon as any color developed in the reaction liquid. The solution was warmed and anhydrous nitrogen swept most of the excess hydrogen chloride out of the reaction flask. The chloride was placed on the Rotovac in an ice bath and residual hydrogen chloride was removed by the water aspirator. The material was pale green and clear without any trace of hydrogen chloride. It was used without any further purification. The 3-chlorocyclopentane produced in this manner was stable over periods up to one week at 0°C. Distillation of 3-chlorocyclopentane increased the rate of decomposition.

3-Chlorocyclopentene, 95% yield, b.p. 37°C.* (37 mm.)

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*Melting points and boiling points in this thesis are uncorrected.

(lit. 128 27-29°C. (20 mm.)).

3-Arylcyclopentenes The preparation of 3-arylcyclopentenes utilized a 1, 4 addition of proper phenyl Grignard reagent to 3-chlorocyclopentene. Grignard reagents (1M.) were prepared by the slow addition of the corresponding phenyl bromide in dry ether to an equimolar amount of magnesium turnings under an anhydrous nitrogen atmosphere. The Grignard was refluxed one hour to insure completeness of reaction. A fifty per cent ether solution of an equimolar amount of 3-chlorocyclopentene was added dropwise to the Grignard reagent cooled in an ice bath. The reaction was stirred for one hour after the addition was complete. After the reaction was poured onto ice and acidified with 10 per cent hydrochloric acid, it was extracted with ether. The extracts were washed with water and dried. After the ether was removed, the olefins were run through a 100 x 40 mm. column of silica gel with chloroform as solvent and eluent. The chloroform was removed and the olefins were vacuum distilled. The 3-arylcyclopentenes decomposed very slowly at room temperature after above purification treatment. Yields of the 3-arylcyclopentene were between seventy and eighty per cent.

3-Phenylcyclopentene, b.p. 50°C. (2.1 mm.)(lit. 129 b.p. 94-96°C. (15 mm.)).

3-(4-methylphenyl) cyclopentene, b.p. 71°C. (1.8 mm.).

3-(4-chlorophenyl) cyclopentene, b.p. 84°C. (1.7 mm.).

3-(3-chlorophenyl) cyclopentene, b.p. 84°C. (2.0 mm.).

3-t-butylcyclopentene, b.p. 50°C. (~5.0 mm.).

1-Arylcyclopentenes The 1-arylcyclopentenes were prepared from the corresponding Grignard reagents and cyclopentanone followed by an acid catalyzed dehydration of the 1-arylcyclopentanols. A 0.5 molar Grignard reagent was prepared under an anhydrous nitrogen atmosphere by adding an equimolar amount of the proper bromobenzene in ether solution to magnesium turnings. After the reaction was refluxed for 30 minutes, an equimolar amount of cyclopentanone was added dropwise with external cooling. The Grignard condensation product was hydrolyzed with 10 per cent hydrochloric acid in ice and extracted with ether. The extracts were washed with water and dried over anhydrous magnesium sulfate. After the ether was removed by distillation, the impure tertiary alcohol was refluxed for two hours with p-toluenesulfonic acid (1 g.) in 50 ml. of benzene. The benzene solution was washed with saturated sodium bicarbonate solution and water respectively and dried over magnesium sulfate. After the removal of the benzene, the olefins were vacuum distilled. Yields were between sixty and eighty per cent for all the 1-arylcyclopentenes.

1-Phenylcyclopentene, b.p. 27°C. (0.6 mm.). (lit. 130 b.p. 118-121°C. (25 mm.)).

1-(4-Methylphenyl) cyclopentene, b.p. 76°C. (0.6 mm.).

1-(4-Chlorophenyl) cyclopentene, b.p. 85°C. (0.7 mm.).

1-(3-Chlorophenyl) cyclopentene, b.p. 81°C. (0.6 mm.).

Trans-2-arylcyclopentanols The trans-2-arylcyclopentanols were prepared by hydroboration followed by basic hydrogen peroxide oxidation of the corresponding 1-arylcyclopentenes using Brown's (118) procedure. Under a dry nitrogen atmosphere 0.05 moles of sodium borohydride was dissolved in 45 ml. of diglyme* with 0.04 moles of the proper 1-arylcyclopentene. After cooling to 0°C., 0.075 moles of boron trifluoride etherate in 10 ml. of diglyme was added cautiously. The reaction was stirred at room temperature for 12 hours before the oxidation step. The solution was cooled to 0°C. and 15 ml. of water added slowly with a vigorous evolution of hydrogen gas. Sodium hydroxide (40 ml. of a 10% solution) was rapidly added before 30 ml. of 30 per cent hydrogen peroxide was added dropwise to the cold mixture. The nitrogen atmosphere was removed as the reaction was allowed to warm to room temperature. It was stirred an additional 6 hours. The alcohol was extracted with ether and the extracts were washed with water and dried over magnesium sulfate. The ether was removed by evaporation and the alcohol was vacuum distilled. All trans-2-arylcyclopentanols were produced in yields between sixty and eighty per cent.

Trans-2-phenylcyclopentanol, b.p. 80°C. (0.25 mm.). (lit. 130 b.p. 110-113°C. (2 mm.)).

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*Diglyme is Bis (2-methoxyethyl) ether.

Trans-2-(4-methylphenyl) cyclopentanol, b.p. 90°C. (0.1 mm.).*

Trans-2-(4-chlorophenyl) cyclopentanol, b.p. 100°C. 0.2 mm.).*

Trans-2-(3-chlorophenyl) cyclopentanol, b.p. 106°C. (0.2 mm.).

Trans-2-deutero-2-phenyl-cyclopentanol The trans-2-deutero-2-phenylcyclopentanol was prepared by modifying Sondheimer's (131, 132) method of hydroboration utilizing lithium aluminum deuteride, boron trifluoride etherate and 1-phenylcyclopentene followed by a basic hydrogen peroxide oxidation. Lithium aluminum deuteride (1 g., 0.024 mole) was dissolved in a solution of 40 ml. of anhydrous ether containing 0.071 moles of the 1-phenylcyclopentene under an anhydrous nitrogen atmosphere. After this mixture was stirred at room temperature for 4 hours, it was cooled to 0°C. and a 80 ml. ether solution containing 0.048 moles of boron trifluoride etherate was added cautiously. The reaction was stirred for 24 hours at room temperature. After the reaction was cooled in an ice bath, 10 ml. of saturated sodium sulfate solution was slowly added with some evolution of hydrogen gas. Anhydrous sodium sulfate (5 g.) was added and the mixture stirred vigorously. The solution was filtered into 50 ml. of tetrahydrofuran which had been freshly distilled from lithium

*Prepared by Dr. Gene F. Morris.

aluminum hydride. The ether was removed by distillation until the equilibrium temperature reached 55°C. The tetrahydrofuran solution was made basic with 25 ml. of 10 per cent sodium hydroxide and was oxidized at 0°C. by a slow addition of 15 ml. of 30 per cent hydrogen peroxide. This reaction was stirred 6 hours at room temperature. The alcohol was extracted with ether and the extracts washed with water and dried over anhydrous magnesium sulfate. The ether was removed by distillation and the alcohol was vacuum distilled at the same temperature and pressure recorded for the undeuterated compound.

Deuterium analysis was made by comparing nuclear magnetic resonance spectra of the deuterated and undeuterated compounds. The trans-2-deutero-2-phenylcyclopentanol was greater than 95 per cent deuterated as determined by this procedure.

Trans-2-deutero-2-phenylcyclopentanol, yield 50%, b.p. 80°C. (0.25 mm.).

Cis-2-arylcyclopentanols* Cis-2-arylcyclopentanols were prepared by the reduction of the epoxide synthesized from the appropriate 3-arylcyclopentene. The epoxides were prepared by treatment of the requisite 3-arylcyclopentene with monoperoxyphthalic acid in ether solution. These epoxides were reduced with excess lithium aluminum hydride in refluxing tetrahydrofuran to a mixture of cis and trans-2-arylcyclopentanols. The alcohols were separated on a Nester-

*Prepared by Dr. Gene F. Morris.

Faust Spinning Spiral Distillation Column run at approximately 800 r.p.m. Compositions of fractions from the distillation were monitored by gas phase chromatography using a UCON LB 550X (1:4) on 60/80 mesh regular W Chromosorb at a temperature of about 150-170°C.

Cis-2-phenylcyclopentanol, b.p. 65°C. (0.15 mm.). (lit. 133 63-63.7°C. (0.1 mm.)).

Cis-2-(4-methylphenyl) cyclopentanol, b.p. 74-75°C. (0.1 mm.).

Cis-2-(4-chlorophenyl) cyclopentanol, b.p. 85°C. (0.2 mm.).

Cis-2-(3-chlorophenyl) cyclopentanol, b.p. 90-91°C. (0.1 mm.).

Cis and trans-2-arylcyclopentyl p-toluenesulfonates

The 2-arylcyclopentyl p-toluenesulfonates were prepared from the corresponding 2-arylcyclopentanols by the Tipson (134) procedure. The proper alcohol (0.02 mole) was dissolved in 30 ml. of dry pyridine and the solution cooled to 0°C. in an ice bath. p-Toluenesulfonyl chloride (1.5 molar equivalents) was added rapidly and swirled into solution. The reaction was placed in the refrigerator (5°C.) for 3 days. During this time a precipitate of pyridine hydrochloride appeared. The mixture was poured into ice water and the product crystallized immediately. It was filtered and washed with 10 per cent hydrochloric acid and water. The solid was dissolved in ether and dried over anhydrous magnesium sulfate. The p-toluenesulfonates were recrystallized five times from

ether-pentane solvent mixture and dried *in vacuo* at room temperature for 8 to 12 hours to remove the last traces of solvent. Yields in all cases were better than seventy-five per cent.

Trans-2-phenylcyclopentyl *p*-toluenesulfonate, m.p. 68°C.* *Anal*. Calcd. for $C_{18}H_{20}SO_3$: C, 68.32; H, 6.37; S, 10.14. Found: C, 68.39; H, 6.31; S, 10.11.

Trans-2-deutero-2-phenylcyclopentyl *p*-toluenesulfonate, m.p. 68°C.

Trans-2-(3-chlorophenyl) cyclopentyl *p*-toluenesulfonate, m.p. 55°C. *Anal*. Calcd. for $C_{18}H_{19}SO_3Cl$: C, 61.61; H, 5.46. Found: C, 61.23; H, 5.35.

Trans-2-(4-chlorophenyl) cyclopentyl *p*-toluenesulfonate, m.p 92°C. *Anal*. Calcd. for $C_{18}H_{19}SO_3Cl$: C, 61.61; H, 5.46. Found: C, 61.50; H, 5.42.

Trans-2-(4-methylphenyl) cyclopentyl *p*-toluenesulfonate, m.p. 88°C. *Anal*. Calcd. for $C_{19}H_{22}SO_3$: C, 69.06; H, 6.71. Found: C, 68.68; H, 6.67.

Cis-2-phenylcyclopentyl *p*-toluenesulfonate, m.p. 97°C. *Anal*. Calcd. for $C_{18}H_{20}SO_3$: C, 68.32; H, 6.37; S, 10.14. Found: C, 68.18; H, 6.25;S,9.97.

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*Melting points were determined on a Fisher-Johns Melting Point Apparatus.

**Decompose slowly with storage at room temperature but are stable at -5°C. for an indefinite period.

Cis-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate, m.p. 81°C. Anal. Calcd. for $C_{18}H_{19}SO_3Cl$: C, 61.61; H, 5.46. Found: C, 61.81; H, 5.68.

Cis-2-(4-chlorophenyl) p-toluenesulfonate, m.p. 108°C. Anal. Calcd. for $C_{18}H_{19}SO_3Cl$: C, 61.61; H, 5.46. Found: C, 61.75; H, 5.44.

Cis-2-(4-methylphenyl) cyclopentyl p-toluenesulfonate,* m.p. 89°C. Anal. Calcd. for $C_{19}H_{22}SO_3$: C, 69.06; H, 6.71. Found: C, 68.81; H, 6.70.

2-Phenylethyl p-toluenesulfonate,** m.p. 38°C. (lit. 6 m.p. 38.5-39°C.).

Purification of materials

Anhydrous ethanol Absolute ethanol was distilled and the middle fraction collected. Freshly cut sodium (5 g.) reacted with the ethanol and the middle fraction collected from a second distillation. The method of Manske (135) was employed to remove the last trace of water from the ethanol. The center cut of the distillation from sodium ethoxide and diethyl phthalate was distilled again from sodium.

Anhydrous tert-butanol Tert-butanol (Eastman Kodak White Label) was fractionally distilled, a sharp center fraction being taken, b.p. 83°C. (1 atm.). This sample was

*Decompose slowly with storage at room temperature but are stable at -5°C. for an indefinite period.

**Prepared by J. Beckman and recrystallized four times by the author.

then distilled at least four times from clean metallic sodium under anhydrous conditions with only the middle fraction being carried over to the next distillation. The metallic sodium (approximately 5 g./liter of t-butanol) was cleaned of all oxides, washed with pentane and warm t-butanol before being placed in the partially purified t-butanol. The all glass distillation apparatus was cleaned with HF before use and no grease was used.

Potassium t-butoxide Potassium metal was cut clean of all oxides and washed in pentane twice. This clean potassium was cut into 0.5 g. cubes and these were melted in hot t-butanol. After reacting approximately 30 seconds in the hot t-butanol the potassium "ball" was removed with a porcelain spoon and frozen in t-butanol at 25°C. The "balls" of potassium metal were rinsed in purified t-butanol and placed in the pure, anhydrous t-butanol and allowed to dissolve under anhydrous conditions. The clear and colorless potassium t-butoxide-t-butanol solution remained clear and colorless under anhydrous conditions for an indefinite time at any temperature between 20° and 50°C.

Procedures and equipment

Isomerization of cyclopentenes* 3-Phenylcyclopentene (0.3108 g., 0.043 mole) was weighed into a 50 ml. volumetric

*Experiment done by Dr. Gene F. Morris.

flask. The olefin was held at 50°C. for 36 hours in 50 ml. of approximately 0.1N potassium t-butoxide-t-butanol solution. The ultraviolet absorption at the maximum of 1-phenylcyclopentene (256.5 mu.) was measured before and after the treatment. There was no change in absorption within experimental error.

A_{Before} = 0.165* at 1/100 dilution with 95% ethanol

A_{After} = 0.177 at 1/100 dilution with 95% ethanol

Analysis of products of the second order elimination reactions

A. Gas phase chromatographic analysis The 2-arylcyclopentyl p-toluenesulfonate (0.0025 moles) was weighed into a 50 ml. volumetric flask. The compound was dissolved in 50 ml. of approximately 0.1M. potassium t-butoxide-t-butanol solution and allowed to react for ten half lives at the reaction temperature. The contents of the volumetric flask then were poured into ice water and extracted with ether. After drying the organic layer over anhydrous magnesium sulfate, the products and solvent were gas chromatographed on a one meter column of UCON LB 550X 1:4 on 60/80 mesh Reg. W Chromosorb at 170°C.

B. Ultraviolet spectral analysis A five milliliter aliquot of a reaction mixture was diluted 1/100

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*Ultraviolet spectra measured with the Beckman DK2a Recording Spectrophotometer.

with 95% ethanol and the ultraviolet absorbance was measured at the maximum of the appropriate 1-arylcyclopentene. Using previously determined molar extinction coefficients, the amount of 1-arylcyclopentene produced can be calculated and compared with the amount of p-toluenesulfonate reacted which was determined titrimetrically at the same reaction time.

Ultraviolet spectra of 1-arylcyclopentenes Molar extinction coefficients were determined in 95 per cent ethanol using a Beckman DK2a recording spectrometer.

1-phenylcyclopentene, 14,710 at 256.5 mμ.

1-(4-methylphenyl) cyclopentene, 17,820 at 258.9 mμ.

1-(4-chlorophenyl) cyclopentene, 17,680 at 261.3 mμ.

1-(3-chlorophenyl) cyclopentene, 14,680 at 259.5 mμ.

Measurement of reaction rates

Second order base catalyzed elimination reactions A solution 0.05 molar in p-toluenesulfonate and approximately 0.1M. in base was prepared in the following manner. The desired compound (0.0025 moles) was weighed accurately into a 50 ml. volumetric flask. After equilibration at the reaction temperature, it was diluted to the calibration mark of the volumetric flask with 0.1 molar base. Kinetic runs were made at 30°, 50° and 70°C. and all solutions were equilibrated and pipeted at those temperatures.

The kinetics were measured by quenching a 5 ml. aliquot in 50 ml. of distilled water and titrating the excess base with standard hydrochloric acid. Infinity points were taken

experimentally and checked well with calculated values. The base was standardized by this procedure at each reaction temperature.

All rates were second order and the integrated form of the second order rate equation was applied to the data. Rates were calculated by taking the average of the individual rates calculated from each experimental point.

$$k = \frac{2.303}{(a-b)t} \log \frac{b(a-x)}{a(b-x)} \qquad (13)$$

Standardization of .1N hydrochloric acid The 0.1N. hydrochloric acid was standardized by J. Beckman against primary standard sodium carbonate using the methyl red procedure (136).

Psuedo first order base catalyzed elimination reactions A solution 0.005 molar in desired compound and 0.1 or 0.3 molar in base was prepared in the following manner. The proper p-toluenesulfonate (0.00025 moles) was weighed accurately into a 50 ml. volumetric flask and placed in the constant temperature bath. After equilibration of base at the reaction temperature, the volumetric flask was filled to the calibration mark and shaken until homogeneity was observed.

The kinetics were followed by quenching a 5 ml. aliquot in 40 ml. of 95% ethanol in a 50 ml. volumetric flask. After diluting to the calibration mark and shaking, the solution was diluted 1:10 with 95 per cent ethanol in a 50 ml. volumetric flask. The olefin concentration of this dilution was measured

by ultraviolet spectrometry.

All rates were psuedo first order and were calculated from a modified integrated form of the first order rate equation. Rates were calculated by taking the average of the individual rates calculated from each point.

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{A^{\infty}-A_o}{A^{\infty}-A_t} \qquad (14)$$

The Hammett equation (42) was applied to the data. Log k/k_o was plotted versus σ and the slope, ρ, was obtained by the method of least squares.

Ethanol-potassium-t-butoxide-t-butanol solvent base system The base was weighed accurately and anhydrous ethanol was added and the solution reweighed. All these solvent systems were recorded as per cent weight of ethanol added. The base concentrated was measured by taking a 5 ml. aliquot at the reaction temperature and titrating it with standard acid.

Kinetic data

Base-promoted second order elimination reactions rates The rates of the base-promoted second order elimination reaction of the 2-arylcyclopentyl p-toluenesulfonates in various base-solvent systems are reported in Tables 24 through 40.* The initial concentrations of substrate and base are included.

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*The major part of the kinetic data was obtained from Dr. Gene F. Morris.

Table 24. Rate of reaction of trans-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^4$ (liter $mole^{-1} sec.^{-1}$)
0	6.70	--
8182	6.21	3.97
14782	5.98	3.73
24863	5.73	3.68
Average rate[b]		3.79 ± 0.12

[a] N_{HCl} = 0.1005; conc. of p-toluenesulfonate = 0.0290 M.; conc. of base = 0.1347 M.

[b] Yield of 1-olefin is 99% by U.V.

Table 25. Rate of reaction of trans-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^4$ (liter $mole^{-1} sec.^{-1}$)
0	4.13	--
1886	4.06	2.97
6760	3.90	2.94
14783	3.68	2.98
24902	3.49	2.86
35337	3.33	2.86
65599	3.03	2.91
80527	2.93	3.02
Average rate		2.93 ± 0.05

[a] N_{HCl} = 0.1086; conc. of p-toluenesulfonate = 0.0315 M.; conc. of base = 0.0897 M.

Table 26. Rate of reaction of *trans*-2-phenylcyclopentyl *p*-toluenesulfonate in potassium *t*-butoxide-*t*-butanol solution at 50°C. (Poor base)

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^4$ (liter $mole^{-1}$ $sec.^{-1}$)
0	4.74	--
8959	4.45	2.16
17057	4.20	2.41
26791	4.01	2.31
41600	3.77	2.32
74690	3.44	2.33
Average rate		2.31 $\pm$ 0.06

[a] N_{HCl} = 0.1005; conc. of *p*-toluenesulfonate = 0.0349 M.; conc. of base = 0.0953 M.

Table 27. Rate of reaction of trans-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 30°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^5$ (liter $mole^{-1} sec.^{-1}$)
0	4.90	--
64692	4.48	5.49
87961	4.39	5.19
146453	4.14	5.59
176436	4.06	5.31
Average rate[b]		5.39 ± 0.15

[a] N_{HCl} = 0.1086; conc. of p-toluenesulfonate = 0.0302 M.; conc. of base = 0.1064 M.

[b] Yield of 1-olefin is 87.7% by G.P.C. (3-olefin = 12.3%).

Table 28. Rate of reaction of trans-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 30°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^5$ (liter $mole^{-1} sec.^{-1}$)
0	6.79	--
43324	6.40	5.33
80109	6.14	5.56
128553	5.89	5.74
166414	5.75	5.83
Average rate[b]		5.61 ± 0.17

[a] N_{HCl} = 0.1005; conc. of p-toluenesulfonate = 0.0300 M.; conc. of base = 0.1365 M.

[b] Yield of 1-olefin is 100% by U.V.

Table 29. Rate of reaction of trans-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol at 70°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^3$ (liter $mole^{-1}$ $sec.^{-1}$)
0	4.69	--
1156	4.36	1.66
2369	4.08	1.75
3655	3.85	1.78
5154	3.67	1.73
6969	3.48	1.76
8729	3.33	1.82
Average rate[b]		1.75 ± 0.04

[a] N_{HCl} = 0.1086; conc. of p-toluenesulfonate = 0.0401 M.; of base = 0.1019 M.

[b] Yield of 1-olefin 76.9% or 88.8% by G.P.C. (3-olefin = 23.1% or 11.2%).

Table 30. Rate of reaction of trans-2-phenylcyclopentyl p-toluenesulfonate in potassium hydroxide[a]-t-butanol solution at 50°C.

Time elapsed (Sec.)	Volume of titrant[b] (ml.)	$k_2 \times 10^4$ (liter $mole^{-1} sec.^{-1}$)
0	4.76	--
2643	4.66	2.48
6591	4.54	2.34
16655	4.29	2.27
70000	3.61	2.30
Average rate		2.35 ± 0.07

[a]Distilled water (0.0837 g.) was added to 50 ml. of 0.1050 M. potassium t-butoxide-t-butanol solution. Water equivalent to the potassium concentration is 0.0955 g.

[b]N_{HCl} = 0.1086; conc. of p-toluenesulfonate = 0.0330 M.; conc. of base = 0.1034 M.

Table 31. Rate of reaction of trans-2-deutero-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^4$ (liter $mole^{-1} sec.^{-1}$)
0	3.90	--
24864	3.66	7.59
68983	3.30	8.28
99878	3.16	7.74
158257	2.92	7.69
239014	2.70	7.69
334690	2.50	8.35
Average rate		7.88 ± 0.22

[a] N_{HCl} = 0.1086; conc. of p-toluenesulfonate = 0.0365 M.; conc. of base = 0.0847 M.

Table 32. Rate of reaction of trans-2-deutero-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C. (Second determination)

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^5$ (liter $mole^{-1} sec.^{-1}$)
0	4.21	--
43380	3.84	7.84
76140	3.64	7.81
135720	3.36	8.15
158700	3.26	8.59
216900	3.16	7.80
246280	3.13	7.34
Average rate		7.92 ± 0.30

[a] N_{HCl} = 0.1086; conc. of p-toluenesulfonate = 0.0311 M.; conc. of base = 0.0914 M.

Table 33. Rate of reaction of trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^3$ (liter $mole^{-1} sec.^{-1}$)
0	5.78	--
797	5.26	3.72
1549	4.94	3.68
2209	4.77	3.48
2961	4.59	3.68
3828	4.48	3.32
Average rate[b]		3.58 ± 0.14

[a] N_{HCl} = 0.1086; conc. of p-toluenesulfonate = 0.0423 M.; conc. of base = 0.1255 M.

[b] Infinity point was higher than the calculated value by a significant amount.

Table 34. Rate of reaction of trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in potassium ethoxide[a] in t-butanol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[b] (ml.)	$k_2 \times 10^3$ (liter $mole^{-1}$ $sec.^{-1}$)
0	5.64	--
772	5.36	1.91
1724	5.08	1.94
2543	4.90	1.92
3539	4.76	1.79
4503	4.63	1.76
5553	4.52	1.72
Average rate[c]		1.84 ± 0.08

[a]Two ml. of absolute ethanol was added to 48 ml. of 0.1346 M. potassium t-butoxide-t-butanol solution.

[b]N_{HCl} = 0.1086; conc. of p-toluenesulfonate = 0.0378 M.; conc. of base = 0.1225 M.

[c]Infinity point much lower than calculated infinity point.

Table 35. Rate of reaction of trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in sodium ethoxide in ethanol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^5$ (liter $mole^{-1} sec.^{-1}$)
0	4.76	--
23872	4.49	5.95
72855	4.03	6.38
155812	3.57	6.30
Average rate		6.21 ± 0.17

[a] N_{HCl} = 0.1086; conc. of p-toluenesulfonate = 0.0448 M.; conc. of base = 0.1034 M.

Table 36. Rate of reaction of trans-2-(4-chlorophenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^3$ (liter $mole^{-1} sec.^{-1}$)
0	4.80	--
531	4.62	1.53
1246	4.42	1.48
2210	4.21	1.41
3422	4.00	1.35
5144	3.78	1.28
7327	3.53	1.28
Average rate		1.39 ± 0.08

[a] N_{HCl} = 0.1086; conc. of p-toluenesulfonate = 0.0488 M.; conc. of base = 0.1043 M.

Table 37. Rate of reaction of *trans*-2-(4-chlorophenyl) cyclopentyl *p*-toluenesulfonate in potassium *t*-butoxide-*t*-butanol solution at 50°C. (Second determination)

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^3$ (liter $mole^{-1}$ $sec.^{-1}$)
0	4.74	--
977	4.45	1.48
2170	4.20	1.37
3315	4.00	1.34
5328	3.72	1.32
7544	3.53	1.29
14856	3.08	1.22
Average rate		1.34 ± 0.06

[a] N_{HCl} = 0.1086; conc. of *p*-toluenesulfonate = 0.0471 M.; conc. of base = 0.1030 M.

Table 38. Rate of reaction of trans-2-(4-methylphenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^4$ (liter $mole^{-1}$ $sec.^{-1}$)
0	5.76	--
4396	5.65	1.34
12327	5.47	1.36
21383	5.27	1.46
39678	4.99	1.44
64990	4.73	1.41
98617	4.49	1.44
Average rate[b]		1.41 ± 0.04

[a] N_{HCl} = 0.1005; conc. of p-toluenesulfonate = 0.0338 M.; conc. of base = 0.1158 M.

[b] Yield of 1-olefin is 81.8% by G.P.C. (3-olefin = 18.2%).

Table 39. Rate of reaction of cis-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^3$ (liter $mole^{-1} sec.^{-1}$)
0	4.49	--
1147	4.12	3.21
1738	3.98	3.20
2366	3.85	3.26
3151	3.73	3.23
4379	3.59	3.21
5482	3.50	3.19
Average rate[b]		3.22 ± 0.02

[a] N_{HCl} = 0.1086; conc. of p-toluenesulfonate = 0.0975 M.; conc. of base = 0.0281 M.

[b] Yield of 1-olefin is 100% by G.P.C.

Table 40. Rate of reaction of cis-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 30°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^4$ (liter $mole^{-1}$ $sec.^{-1}$)
0	4.53	--
2417	4.38	6.14
7503	4.17	5.61
9725	4.09	5.66
12509	4.01	5.59
46520	3.54	6.15
72700	3.47	6.11
Average rate		5.88 ± 0.26

[a] N_{HCl} = 0.1086; conc. of p-toluenesulfonate = 0.0236 M.; conc. of base = 0.0984 M.

Base-promoted psuedo first order elimination reaction rates The rates of the base-promoted psuedo first order elimination reaction of the 2-arylcyclopentyl p-toluenesulfonates in various base-solvent systems are reported in Tables 41 through 71. The initial concentrations of substrate, base and infinity absorption value calculated from extinction coefficients are included.

Table 41. Rate of reaction of trans-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^5$ (sec.$^{-1}$)
0	0.038	--
4,764	0.132	2.98
10,280	0.222	2.92
15,516	0.292	2.85
27,211	0.414	2.77
40,254	0.506	2.67
56,787	0.593	2.68
299,083	0.748[a]	
Average rate[b]		2.81 ± 0.10

[a]Calculated infinity absorbance = 0.721.

[b]Concentration of base = 0.09550 M.; conc. of p-toluenesulfonate = 4.899×10^{-3} M.

Table 42. Rate of reaction of trans-2-(4-methylphenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^6$ (sec.$^{-1}$)
0	0.047	--
13,345	0.154	10.83
25,670	0.237	10.64
58,577	0.403	10.14
73,542	0.460	9.97
98,247	0.527	9.41
608,729	0.842[a]	--
Average rate[b]		10.2 ± 0.43

[a]Calculated infinity absorbance = 0.863.

[b]Conc. of base = 0.09550 M.; conc. of p-toluenesulfonate = 4.854×10^{-3} M.

Table 43. Rate of reaction of trans-2-(4-chlorophenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.171	--
2,205	0.371	1.29
5,253	0.569	1.25
6,846	0.641	1.23
8,041	0.687	1.22
9,184	0.731	1.24
10,598	0.763	1.19
12,167	0.805	1.20
58,512	0.996[a]	--
Average rate[b]		1.23 ± 0.02

[a]Calculated infinity absorbance = 0.884.

[b]Conc. of base = 0.09550 M.; conc of p-toluenesulfonate = 4.999×10^{-3} M.

Table 44. Rate of reaction of trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.068	--
992	0.267	3.26
2,739	0.499	3.33
5,205	0.658	3.29
6,830	0.707	3.22
8,327	0.738	3.16
9,700	0.752	3.09
10,787	0.760	3.01
27,746	0.788[a]	--
Average rate[b]		3.20 ± 0.09

[a]Calculated infinity absorbance = 0.762.

[b]Conc. of base = 0.09550 M.; conc. of p-toluenesulfonate = 5.193×10^{-3} M.

Table 45. Rate of reaction of trans-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.093	--
1,479	0.206	1.39
3,017	0.302	1.40
5,001	0.397	1.39
7,752	0.495	1.40
10,772	0.563	1.38
14,991	0.627	1.41
43,873	0.700[a]	--
Average rate[b]		1.40 ± 0.01

[a]Calculated infinity absorbance = 0.705.

[b]Conc. of base = 0.3361 M.; conc. of p-toluenesulfonate = 4.791×10^{-3} M.

Table 46. Rate of reaction of trans-2-(4-methylphenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^5$ (sec.$^{-1}$)
0	0.062	--
4,945	0.237	5.52
10,103	0.373	5.47
14,979	0.464	5.31
21,627	0.570	5.46
32,656	0.660	5.19
191,541	0.795[a]	--
Average rate[b]		5.39 ± 0.11

[a]Calculated infinity absorbance = 0.916.

[b]Conc. of base = 0.3361 M.; conc. of p-toluenesulfonate = 5.139×10^{-3} M.

Table 47. Rate of reaction of trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^3$ (sec.$^{-1}$)
0	0.145	--
403	0.401	1.45
577	0.477	1.48
905	0.577	1.52
1,206	0.631	1.52
1,499	0.666	1.55
2,095	0.697	1.48
9,208	0.723[a]	--
Average rate[b]		1.50 ± 0.03

[a]Calculated infinity absorbance = 0.712.

[b]Conc. of base = 0.3361 M.; conc. of p-toluenesulfonate = 4.851×10^{-3} M.

Table 48. Rate of reaction of *trans*-2-phenylcyclopentyl *p*-toluenesulfonate in potassium *t*-butoxide-*t*-butanol solution at 30.3°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^6$ ($sec.^{-1}$)
0	0.066	--
35,973	0.164	4.81
92,266	0.272	4.47
157,856	0.371	4.39
241,473	0.463	4.36
365,791	0.548	4.27
505,344	0.599	4.10
2,490,000	0.676[a]	--
Average rate[b]		4.40 ± 0.16

[a]Calculated infinity absorbance = 0.695.

[b]Conc. of base = 0.09590 M.; conc. of *p*-toluenesulfonate = 4.728×10^{-3} M.

Table 49. Rate of reaction of trans-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 30.3°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^5$ (sec.$^{-1}$)
0	0.051	--
4,300	0.121	2.55
9,414	0.194	2.54
18,035	0.300	2.56
37,247	0.462	2.53
55,599	0.561	2.55
108,214	0.679	2.50
371,400	0.724[a]	--
Average rate[b]		2.54 ± 0.02

[a]Calculated infinity absorbance = 0.730.

[b]Conc. of base = 0.3405 M.; conc. of p-toluenesulfonate = 4.962×10^{-3} M.

Table 50. Rate of reaction of trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol - 0.96 weight per cent ethanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^3$ (sec.$^{-1}$)
0	0.169	--
411	0.403	1.21
605	0.486	1.23
849	0.558	1.21
1,067	0.608	1.21
1,494	0.676	1.22
10,638	0.774[a]	--
Average rate[b]		1.22 ± 0.01

[a]Calculated infinity absorbance = 0.735.

[b]Conc. of base = 0.3273 M.; conc. of p-toluenesulfonate = 5.005×10^{-3} M.

Table 51. Rate of reaction of trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol - 1.94 weight per cent ethanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^3$ (sec.$^{-1}$)
0	0.150	--
473	0.385	1.05
745	0.478	1.06
1,024	0.545	1.04
1,395	0.615	1.06
16,559	0.752[a]	--
Average rate[b]		1.05 ± 0.01

[a]Calculated infinity absorbance = 0.709.

[b]Conc. of base = 0.3277 M.; conc. of p-toluenesulfonate = $4,828 \times 10^{-3}$ M.

Table 52. Rate of reaction of trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol - 3.88 weight per cent ethanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.163	--
481	0.353	7.95
710	0.422	7.99
1,100	0.517	8.15
1,496	0.588	8.29
2,150	0.662	8.37
3,132	0.715	8.21
10,319	0.761[a]	--
Average rate[b]		8.16 ± 0.13

[a]Calculated infinity absorbance = 0.719.

[b]Conc. of base = 0.3185 M ; conc. of p-toluenesulfonate = $4,897 \times 10^{-3}$ M.

Table 53. Rate of reaction of trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol - 9.80 weight per cent ethanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.117	--
300	0.199	4.49
597	0.272	4.56
903	0.336	4.54
1,260	0.403	4.59
1,780	0.485	4.68
2,663	0.577	4.61
3,892	0.652	4.43
15,000	0.768[a]	--
Average rate[b]		4.56 ± 0.06

[a]Calculated infinity absorbance = 0.727.

[b]Conc. of base = 0.3019 M.; conc. of p-toluenesulfonate = 4.954×10^{-3} M.

Table 54. Rate or reaction of trans-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in sodium ethoxide-ethanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^6$ ($sec.^{-1}$)
0	0.063	--
35,459	0.157	7.97
96,782	0.264	7.66
162,299	0.323	6.95
245,843	0.363	6.16
2,490,619	0.448[a]	--
Average rate[b]		7.18 ± 0.63

[a]Calculated infinity absorbance = 0.690.

[b]Conc. of base = 0.1852 M.; conc. of p-toluenesulfonate = 4.703×10^{-3} M.

Table 55. Rate of reaction of cis-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ ($sec.^{-1}$)
0	0.164	--
643	0.252	2.64
1,247	0.317	2.54
1,844	0.380	2.62
2,420	0.433	2.68
3,145	0.485	2.68
3,859	0.525	2.65
55,566	0.728[a]	--
Average rate[b]		2.64 ± 0.04

[a]Calculated infinity absorbance = 0.698.

[b]Conc. of base = 0.09550 M.; conc. of p-toluenesulfonate = 4.747×10^{-3} M.

Table 56. Rate of reaction of cis-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C. (Second determination)

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.130	--
1,186	0.306	2.57
1,866	0.388	2.61
2,466	0.455	2.69
3,395	0.531	2.69
4,669	0.605	2.64
27,077	0.800[a]	--
Average rate[b]		2.64 ± 0.04

[a]Calculated infinity absorbance = 0.764.

[b]Conc. of base = 0.09550 M.; conc. of p-toluenesulfonate = 5.196×10^{-3} M.

Table 57. Rate of reaction of cis-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 30.3°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^5$ (sec.$^{-1}$)
0	0.115	--
2,192	0.189	5.47
3,916	0.239	5.36
8,270	0.349	5.35
16,376	0.500	5.41
25,468	0.607	5.46
40,558	0.696	5.38
114,248	0.770[a]	--
Average rate[b]		5.40 ± 0.04

[a]Calculated infinity absorbance = 0.755.

[b]Conc. of base = 0.09590 M.; conc. of p-toluenesulfonate = 5.133×10^{-3} M.

Table 58. Rate of reaction of cis-2-(4-methylphenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.087	--
507	0.130	1.10
1,048	0.183	1.23
1,962	0.251	1.18
2,890	0.316	1.17
4,339	0.409	1.19
6,387	0.509	1.18
10,518	0.650	1.17
68,069	0.883[a]	--
Average rate[b]		1.17 ± 0.02

[a]Calculated infinity absorbance = 0.867.

[b]Conc. of base = 0.09550 M.; conc. of p-toluenesulfonate = 4.866×10^{-3} M.

Table 59. Rate of reaction of cis-2-(4-methylphenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C. (Second determination)

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.090	--
304	0.117	1.18
1,003	0.178	1.22
2,003	0.264	1.28
2,998	0.333	1.27
3,995	0.395	1.27
6,008	0.501	1.28
10,389	0.646	1.24
80,033	0.857[a]	--
Average rate[b]		1.25 ± 0.03

[a]Calculated infinity absorbance = 0.846.

[b]Conc. of base = 0.09550 M.; conc. of p-toluenesulfonate = 4.745×10^{-3} M.

Table 60. Rate of reaction of cis-2-(4-chlorophenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.133	--
536	0.307	4.66
899	0.407	4.75
1,290	0.500	4.86
1,812	0.593	4.84
2,420	0.673	4.78
3,320	0.767	4.92
22,220	0.921[a]	--
Average rate[b]		4.80 ± 0.07

[a]Calculated infinity absorbance = 0.838.

[b]Conc. of base = 0.09550 M.; conc. of p-toluenesulfonate = 4.737×10^{-3} M.

Table 61. Rate of reaction of cis-2-(4-chlorophenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C. (Second determination)

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.412	--
538	0.539	4.33
1,005	0.628	4.34
1,507	0.704	4.31
2,016	0.768	4.34
2,687	0.838	4.45
3,596	0.891	4.26
66,501	1.023[a]	--
Average rate[b]		4.34 ± 0.04

[a]Calculated infinity absorbance = 0.884.

[b]Conc. of base = 0.09550 M.; conc. of p-toluenesulfonate = 4.999×10^{-3} M.

Table 62. Rates of reaction of cis-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.138	--
518	0.348	8.16
745	0.420	8.35
1,006	0.489	8.54
1,372	0.559	8.57
1,937	0.631	8.56
3,144	0.708	8.74
29,133	0.747[a]	--
Average rate[b]		8.48 ± 0.16

[a]Calculated infinity absorbance = 0.738.

[b]Conc. of base = 0.09550 M.; conc. of p-toluenesulfonate = 5.028×10^{-3} M.

Table 63. Rate of reaction of cis-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C. (Second determination)

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.162	--
457	0.344	8.36
798	0.442	8.41
1,111	0.512	8.50
1,502	0.575	8.49
2,003	0.633	8.62
3,008	0.688	8.31
56,015	0.735[a]	--
Average rate[b]		8.45 ± 0.09

[a]Calculated infinity absorbance = 0.719.

[b]Conc. of base = 0.09550 M.; conc. of p-toluenesulfonate = 4.897×10^{-3} M.

Table 64. Rate of reaction of cis-2-phenylcyclopentyl p-toluenesulfonate in sodium ethoxide-ethanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.117	--
933	0.305	3.96
2,584	0.514	4.08
3,619	0.598	4.12
20,175	0.726[a]	--
Average rate[b]		4.05 ± 0.06

[a]Calculated infinity absorbance = 0.727.

[b]Conc. of base = 0.1720 M.; conc. of p-toluenesulfonate = 4.943×10^{-3} M.

Table 65. Rate of reaction of cis-2-(4-methylphenyl) cyclopentyl p-toluenesulfonate in sodium ethoxide-ethanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ ($sec.^{-1}$)
0	0.175	--
406	0.256	3.15
795	0.327	3.21
1,362	0.417	3.26
2,110	0.508	3.22
3,290	0.613	3.18
4,292	0.683	3.25
6,101	0.755	3.21
20,474	0.850[a]	--
Average rate[b]		3.21 ± 0.03

[a]Calculated infinity absorbance = 0.961.

[b]Conc. of base = 0.1720 M.; conc. of p-toluenesulfonate = 5.393×10^{-3} M.

Table 66. Rate of reaction of cis-2-(4-chlorophenyl) cyclopentyl p-toluenesulfonate in sodium ethoxide-ethanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.226	--
256	0.361	7.90
1,201	0.676	7.85
1,508	0.740	7.93
1,901	0.802	8.00
2,401	0.854	7.96
10,283	0.963[a]	--
Average rate[b]		7.93 ± 0.04

[a]Calculated infinity absorbance = 0.863.

[b]Conc. of base = 0.1720 M.; conc. of p-toluenesulfonate = 4.879×10^{-3} M.

Table 67. Rate of reaction of cis-2-(3-chlorophenyl) cyclopentyl p-toluenesulfonate in sodium ethoxide-ethanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^3$ ($sec.^{-1}$)
0	0.144	--
444	0.344	1.00
724	0.439	1.04
999	0.510	1.07
1,382	0.580	1.10
1,909	0.630	1.07
2,530	0.667	1.09
9.612	0.702[a]	--
Average rate[b]		1.05 ± 0.03

[a]Calculated infinity absorbance = 0.688.

[b]Conc. of base = 0.1720 M.; conc. of p-toluenesulfonate = 4.686×10^{-3} M.

Table 68. Rate of reaction of cis-2-(4-methylphenyl) cyclopentyl p-toluenesulfonate in sodium ethoxide-ethanol solution at 50°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.132	--
612	0.428	8.51
820	0.502	8.64
1,053	0.571	8.76
1,372	0.642	8.77
1,815	0.718	8.98
8,526	0.861[a]	--
Average rate[b]		8.73 ± 0.13

[a]Calculated infinity absorbance = 0.897.

[b]Conc. of base = 0.5101 M.; conc. of p-toluenesulfonate = 5.036×10^{-3} M.

Table 69. Rate of reaction of 2-phenylethyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 30.3°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.059	--
1,123	0.176	1.84
2,006	0.251	1.81
2,557	0.293	1.82
42,650	0.688[a]	--
Average rate[b]		1.82 ± 0.01

[a]Calculated infinity absorbance = 0.657 using 13,800 as the extinction coefficient at 248 mμ. (6).

[b]Conc. of base = 0.09590 M.; conc. of p-toluenesulfonate = 4.762×10^{-3} M.

Table 70. Rate of reaction of 2-phenylethyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 30.3°C. (Second determination)

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.121	--
533	0.187	2.08
1,042	0.231	1.84
2,115	0.318	1.78
3,429	0.410	1.79
5,326	0.509	1.79
7,757	0.590	1.77
11,558	0.663	1.62
41,196	0.750[a]	--
Average rate[b]		1.81 ± 0.09

[a]Calculated infinity absorbance = 0.713.

[b]Conc. of base = 0.09590 M.; conc. of p-toluenesulfonate = 5.167×10^{-3} M.

Table 71. Rate of reaction of 2-phenylethyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 30.3°C.

Time elapsed (sec.)	Absorbance	$k_1 \times 10^4$ (sec.$^{-1}$)
0	0.103	--
388	0.233	7.25
626	0.295	7.19
848	0.346	7.23
1,221	0.416	7.31
1,777	0.487	7.26
2,636	0.555	7.27
11,576	0.633[a]	--
Average rate[b]		7.25 ± 0.03

[a]Calculated infinity absorbance = 0.612.

[b]Conc. of base = 0.3405 M.; conc. of p-toluenesulfonate = 4.436×10^{-3} M.

Part II: Beta Elimination Studies of 3-Phenylcyclopentyl Bromides and p-Toluenesulfonates

Preparation and purification of materials

Attempted preparation of 2-phenylcyclopentyl bromide

Five attempts were made to synthesize 2-phenylcyclopentyl bromide from phenylcyclopentenes by free radical addition of hydrogen bromide and all resulted in failure.

A. 1-Phenylcyclopentene (10 g.) in 100 ml. of purified pentane was refluxed in a quartz tube under ultraviolet light for two hours with anhydrous hydrogen bromide bubbled through the solution (137). The solution was poured on solid sodium carbonate before the pentane was removed and olefin distilled.

B. Procedure A was used except hexane was used as solvent in order to increase the temperature of the reaction.

C. Heating the olefin with benzoyl peroxide and dry hydrogen bromide (137) at the reflux temperature of heptane also failed to produce any stable bromides.

D. Cis-2-phenylcyclopentyl p-toluenesulfonate (2.3 g.) did not produce trans-2-phenylcyclopentyl bromide when allowed to stand in the dark with lithium bromide in anhydrous acetone.

E. Procedure C was used with 3-phenylcyclopentene for 4 hours at reflux temperature with no addition products isolated.

Preparation of cis and trans-3-phenylcyclopentyl bromide

A mixture of cis and trans-3-phenylcyclopentyl bromide was prepared by the action of anhydrous hydrogen bromide on 3-phenylcyclopentene. Anhydrous hydrogen bromide was bubbled through 10 g. of 3-phenylcyclopentene in 100 ml. of refluxing acetic acid for five hours. After the acetic acid had been removed by distillation, the products were crudely vacuum distilled. The halogen fraction was collected at 72°C. (0.15 mm). The liquid was carefully fractionated on a gold plated spinning band distillation column. By gas chromatographic analysis a separation was obtained between two bromo compounds. (Gas phase chromatograph on a 1 meter column of 1:4 carbowax on 60/80 mesh regular W Chromosorb at 152°C. The lower boiling fraction was not studied further but it was believed to be cis and/or trans-2-phenylcyclopentyl bromides (116, 117). The second fraction was shown to be a mixture of cis and trans-3-phenylcyclopentyl bromides by nuclear magnetic resonance spectra and product analysis of base promoted elimination reaction.

Preparation of cis and trans-3-phenylcyclopentanol

Cis and trans-3-phenylcyclopentanols were prepared by the hydroboration of 3-phenylcyclopentene. The hydroboration procedure has been described previously. The crude product upon gas phase chromatographic analysis (one meter column of 1:3 UCON LB 550X on firebrick at 164°C.) contained the following compounds: cis-2-phenylcyclopentanol 5%, trans-

2-phenylcyclopentanol 60%, and the 3-phenylcyclopentanols 35%. The substances were separated by a vacuum distillation through a 100 cm. spinning band distillation column.

Cis and trans-3-phenylcyclopentanols, b.p. 80°C. (0.13 mm.).

Equilibration of cis and trans-3-phenylcyclopentanols

Equilibration of cis and trans-3-phenylcyclopentanols was achieved by the oxidation of the 3-phenylcyclopentanols produced by the hydroboration reaction followed by reduction of the ketone with lithium aluminum hydride to the alcohols. These reactions were carried out by Gene F. Morris. An equimolar mixture was obtained.

Preparation of cis and trans-3-phenylcyclopentyl acetates

The acetates of cis and trans-3-phenylcyclopentanols were prepared by the action of acetyl chloride in pyridine-benzene solution. 3-Phenylcyclopentanols (1 g.) 15 ml. benzene, 1 ml. pyridine, and 1 ml. of acetyl chloride stood at room temperature for 2 days. The mixture was poured into ice water and the benzene layer separated and dried. After the careful removal of the benzene on the Rotovac, the remaining liquid was microdistilled.

Infrared spectrum showed that no alcohol remained. Nuclear magnetic resonance spectra and gas phase chromatographic analysis gave crude analysis for the mixture. (Gas phase chromotograph on a 100 meter, 1/8 inch Golay capillary column with a Silicon SE30 liquid phase at 125°C. was used).

Preparation of cis and trans-3-phenylcyclopentyl p-toluenesulfonates The 3-phenylcyclopentyl p-toluenesulfonates were prepared by the Tipson (134) procedure described previously. Fractional crystallization from pentane-ether produced a crystalline p-toluenesulfonate.

Cis or trans-3-phenylcyclopentyl p-toluenesulfonate, m.p. 42°C.

Preparation of cis and trans-3-phenylcyclopentyl-3, 5-dinitrobenzoate The benzoates were prepared in a similar manner to the acetates. 3-Phenylcyclopentanols (10 g.) was reacted with 25 g. of freshly opened 3, 5-dinitrobenzoyl chloride in an anhydrous solution of 200 ml. benzene and 10 ml. of pyridine. This mixture was refluxed for 3 days. The reaction was poured onto ice and the organic layer separated, washed with sodium bicarbonate solution, dried and solvent removed. The esters have not been purified at this time.

Procedures and equipment

Measurements of reaction rates Procedure for the measurement of second order rates has been previously desribed on page 117.

Product analysis of the base-promoted elimination of cis and trans-3-phenylcyclopentyl bromides Measurements of the rate of base-catalyzed elimination reaction of the bromide mixture were stopped and the remaining solution quenched in ice water. This solution was extracted with ether. The

extracts were dried and the ether carefully removed. The remaining bromides were microdistilled and submitted for nuclear magnetic resonance and gas phase chromatographic analysis (one meter column of UCON LB 550X 1:3 on firebrick at 72°C.)

Table 72. Rate of reaction of cis and trans-3-phenylcyclopentyl bromides in potassium t-butoxide-t-butanol solution at 30°C.

Time elapsed (sec.)	Volume of titrant[b] (ml.)	$k \times 10^5$ (liter $mole^{-1}$ $sec.^{-1}$)	$k \times 10^5$ [a] ($sec.^{-1}$)
468	6.19	48.0	--
1,243	6.16	26.9	--
4,852	6.12	9.98	--
18,673	5.98	5.56	4.12
39,332	5.82	4.39	3.68
52,039	5.64	4.22	3.78
83,318	5.50	4.10	3.75
102,208	5.41	3.88	3.59
128,338	5.24	4.00	3.78
153,742	5.18	3.65	3.45
Average rate			3.74 ± 0.14

[a]Time zero = 4,852 sec.; conc. of bromide = 0.0433 M.; conc. of base = 0.1230 M.

[b]N_{HCl} = 0.1005, conc. of bromide = 0.0459 M.; conc. of base = 0.1256 M.

Table 73. Rate of reaction of cis and trans-3-phenylcyclopentyl bromides in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k \times 10^4$ (liter $mole^{-1}$ $sec.^{-1}$)
7,980	6.90	2.15
15,095	6.67	1.97
23,465	6.42	2.00
53,770	5.92	1.94
77,620	5.75	1.81
Average rate		1.97 ± 0.08

[a] N_{HCl} = 0.1005; conc. of bromide = 0.0376 M.; conc. of base = 0.1464 M.

Part III: Beta Eliminations Studies of Cyclopentyl p-Toluenesulfonate and Halides

Preparation and purification of materials

Preparation of cyclopentyl p-toluenesulfonate Tipson's procedure (134) was used in the preparation of cyclopentyl p-toluenesulfonate from cyclopentanol and p-toluenesulfonyl chloride. Cyclopentanol (3 g.) was dissolved in 45 ml. of anhydrous pyridine and the solution was cooled in an ice bath. After 9.9 g. of p-toluenesulfonyl chloride was added rapidly, the mixture was swirled until homogeneous and stored for two days at 5°C. in the refrigerator. During this time, pyridine hydrochloric crystals appeared. The reaction mixture was poured into ice water and the p-toluenesulfonate separated as an oil. The product was extracted with ether. After washing, drying and removing the ether, the cyclopentyl p-toluenesulfonate was crystallized from an ether-pentane solution. It was recrystallized four more times and dried *in vacuo*. The p-toluenesulfonate decomposed slowly at room temperature.

Cyclopentyl p-toluenesulfonate, m.p. 27°C. (lit. 138 m.p. 27°C.).

Cyclopentyl halides

Cyclopentyl chloride Cyclopentyl chloride was prepared by the action of phosphorus trichloride on cyclopentanol. Cyclopentanol (0.08 moles) was cooled to -10°C. in an anhydrous nitrogen atmosphere. Phosphorus trichloride

(0.04 moles) was added slowly to the alcohol with vigorous stirring. After the addition, the reaction was stirred for two hours at 0°C. The solution was then warmed to room temperature and stirred for 6 more hours. The reaction was poured into ice water and extracted with ether. The extracts were washed with saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. After careful removal of the ether by distillation, the chloride was vacuum distilled as a clear, colorless liquid.

Cyclopentyl chloride, b.p. 51°C. (80 mm.); N_D^{23} = 1.4498 (lit. 139 b.p. 111-112°C.; N_D^{25} = 1.4485).

Cyclopentyl bromide Cyclopentyl bromide was prepared by the action of phosphorus tribromide on cyclopentanol following the procedure given for the preparation of cyclopentyl chloride.

Cyclopentyl bromide, b.p. 62°C. (60 mm.). (lit. 139 b.p. 58-58.5°C. (50 mm.)).

Cyclopentyl iodide Cyclopentyl iodide was prepared by the action of sodium iodide on cyclopentyl bromide in anhydrous acetone. (The action of hydroiodic acid on cyclopentanol was unsuccessful using the procedure described for the preparation of cyclopentyl chloride.) Cyclopentyl bromide 0.07 moles was reacted with 0.13 moles of sodium iodide for 30 hours in 100 ml. of refluxing acetone. (The acetone had been dried previously by a distillation from

anhydrous calcium sulfate.) After removal of excess acetone by distillation, solid sodium iodide was removed by filtration. The remaining liquid was taken up in ether and washed with sodium thiosulfate solution and water. After being dried over anhydrous magnesium sulfate, the ether was removed by distillation. The iodide was vacuum distilled and quickly stored in the dark at -10°C. in the freezer. It was fairly stable under these conditions. Before being used, the iodide was shaken with elemental mercury and rapidly vacuum distilled.

Cyclopentyl iodide, b.p. 76°C. (43 mm.); N_D^{23} = 1.5421. (lit. 139 b.p. 65-66°C. (27 mm.), N_D^{25} = 1.5457).

Preparation of cyclopentanol Cyclopentanol was prepared by the reduction of cyclopentanone (Araphoe Chem. Co.) with lithium aluminum hydride. Lithium aluminum hydride (0.06 moles) was dissolved in 100 ml. of anhydrous ether under an anhydrous nitrogen atmosphere. Twenty milliliters of an ether solution containing 0.12 moles of cyclopentanone was added dropwise. After the reaction was stirred five hours, it was cooled in an ice bath and 20 ml. of water was added cautiously. The reaction was made acidic with 10% hydrochloric acid and extracted with ether. The water layer was saturated with sodium chloride because of the high solubility of cyclopentanol in water. After the ether was dried and removed, cyclopentanol was vacuum distilled.

Cyclopentanol, b.p. 52°C. (14 mm.). (lit. 139 139.8-140.4°C.

Procedures and equipment

Measurement of reaction rates

Base catalyzed elimination reactions Kinetics were measured titrametrically previously described on page 117. It was noted that quenching of the sample must be in ice-water due to the high rate of solvolysis of cyclopentyl p-toluenesulfonate in distilled water at room temperature.

Product analysis of base-promoted eliminations of cyclopentyl derivatives The cyclopentyl compound (0.0025 moles) was placed in a 50 ml. volumetric flask. The compound was dissolved in 50 ml. of .1M potassium t-butoxide-t-butanol solution and allowed to react for ten half lives. The contents of the volumetric flask then were poured into ice water and extracted with carbon tetrachloride. After drying the organic layer over anhydrous magnesium sulfate, the products and solvent were gas chromatographed on a one meter column of Apiezon L 1:3 on firebrick at 30°C. and 75°C.

Kinetic data

The rates of the base-catalyzed elimination reactions of cyclopentyl derivatives are reported as follows: The volumes of titrant reported in the second column of each table are the amounts of hydrochloric acid required to neutralize five

milliliter aliquots of the reaction solution. Also included are the normality of the titrant, initial concentrations of cyclopentyl compound and base, per cent olefin, the second order rate constants calculated for each point and the average rate constant.

Table 74. Rate of reaction of cyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^4$ (liter mole^{-1} sec.$^{-1}$)
10,313	5.57	3.86
18,233	5.20	3.85
27,757	4.90	3.88
Average rate[b]		3.86 ± 0.01

[a] N_{HCl} = 0.1005; conc. of p-toluenesulfonate = 0.0426 M.; conc. of base = 0.1280 M.

[b] Product contains > 99% cyclopentene.

Table 75. Rate of reaction of cyclopentyl bromide in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^4$ (liter $mole^{-1}$ $sec.^{-1}$)
18,463	5.69	1.96
28,153	5.40	1.97
39,353	5.17	1.91
65,477	4.79	1.90
75,387	4.67	1.96
Average rate[b]		1.94 ± 0.03[c]

[a] N_{HCl} = 0.1005; conc. of bromide = 0.0469 M.; conc. of base = 0.1312 M.

[b] Product contains > 99% cyclopentene.

[c] Repeat determination gave an average rate = 1.90 ± 0.04 x 10^{-4} liter $mole^{-1}$ $sec.^{-1}$.

Table 76. Rate of reaction of cyclopentyl iodide in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^3$ (liter mole^{-1} sec.$^{-1}$)
1,741	4.65	1.06
4,376	4.20	1.07
9.284	3.67	1.07
12,393	3.46	1.05
17,383	3.22	1.04
25,044	2.98	1.06
Average rate		1.06 ± 0.01

[a] N_{HCl} = 0.1005; conc. of iodide = 0.0486 M.; conc. of base = 0.1015 M.

Table 77. Rate of reaction of cyclopentyl chloride in potassium t-butoxide-t-butanol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^6$ (liter mole^{-1} sec.$^{-1}$)
564,640	4.77	2.52
1,261,193	4.37	2.75
Average rate		2.6 ± 0.1

[a] N_{HCl} = 0.1005; conc. of chloride = 0.0547 M.; conc. of base = 0.1031 M.

Part IV: Beta Elimination Studies of Trans-2-arylcyclohexyl p-Toluenesulfonates

Preparation and purification of materials

Preparation of arylcyclohexyl compounds

1-arylcyclohexenes Procedure is identical with that described for 1-arylcyclopentenes.

1-Phenylcyclohexene, b.p. 81°C. (0.2 mm.)* ** (lit.140 b.p. 55-57°C. (0.15 mm.)).

1-(3-Chlorophenyl) cyclohexene, b.p. 81°C. (0.1 mm.)* (lit. 140 b.p. 78-79°C. (0.1 mm.)).

1-(4-Methoxyphenyl) cyclohexene, b.p. 114°C. (0.1 mm.) m.p. 32°C.* (lit. 140 b.p. 114-118°C. (0.3 mm.), m.p. 32.5-33.5°C.).

1-(3-Trifluoromethylphenyl) cyclohexene, b.p. 70°C. (0.6 mm.).

1-(4-Trifluoromethylphenyl)cyclohexene, b.p. 66°C. (0.3 mm.).

4-t-Butyl-1-phenylcyclohexene, b.p. 105°C. (0.3 mm.).

Trans-2-arylcyclohexanols These compounds were prepared by the procedure described for the preparation of trans-2-arylcyclopentanols.

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*Prepared by D. K. Wedegaertner.

**Further purification by a vacuum distillation from metallic sodium.

Trans-2-Phenylcyclohexanol, b.p. 93°C. (0.2 mm.); m.p. 53°C.* (lit. 121 m.p. 55-57°C.).

Trans-2-(3-Chlorophenyl) cyclohexanol, b.p. 135°C. m.p. 53°C. (0.1 mm.).*

Trans-2-(4-Methoxyphenyl) cyclohexanol, b.p. 114°C. (0.2 mm.) m.p. 60°C.

Trans-2-(3-trifluoromethylphenyl) cyclohexanol, b.p. 85°C. (0.3 mm.).

Trans-2-(4-trifluoromethylphenyl) cyclohexanol, m.p. 96°C. It was crystallized from hexane-ether.*

Trans-5-t-butyl-2-phenylcyclohexanol, b.p. 119°C. (0.3 mm.).

Trans-2-deutero-2-arylcyclohexanols These compounds were prepared by the procedure described for the preparation of the analogous cyclopentyl compounds. Yields of the deuterated alcohols ranged between forty and sixty per cent. The trans-2-deutero-2-arylcyclohexanols were greater than 95 per cent deuterated as determined by nuclear magnetic resonance spectra analysis.

Trans-2-deutero-2-phenylcyclohexanol, b.p 93°C. (0.2 mm.).

Trans-2-deutero-2-(3-trifluoromethylphenyl) cyclohexanol, b.p. 85°C. (0.3 mm.).

Trans-2-deutero-5-t-butyl-2-phenylcyclohexanol, b.p. 119°C. (0.3 mm.).

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*Prepared by D. K Wedegaertner.

Trans-2-arylcyclohexyl p-toluenesulfonates The trans-2-arylcyclohexyl p-toluenesulfonates were prepared from the corresponding trans-2-arylcyclohexanols by the Tipson (134) procedure which has been previously described for the preparation of the 2-arylcyclopentyl p-toluenesulfonate. When the reaction mixture was stored in the refrigerator, the p-toluenesulfonate precipitated with the pyridine hydrochloride. The solid was broken up in ice water, filtered and washed with 10 per cent hydrochloric acid and water. The p-toluenesulfonate was dissolved in chloroform and dried by the distillation of the water-chloroform azeotrope. The trans-2-arylcyclohexyl p-toluenesulfonates were recrystallized from a 3:1 solution of chloroform and ether They were dried in vacuo at 56°C. for 12 hours to remove the last traces of solvent.

Trans-2-phenylcyclohexyl p-toluenesulfonate, m.p. 127°C. (dec.). Anal. Calcd. for $C_{19}H_{22}SO_3$: C, 69.06; H, 6.41; S, 9.71. Found: C, 68.48; H, 6.38; S, 10.22.

Trans-2-deutero-2-phenylcyclohexyl p-toluenesulfonate, m.p. 127°C. (dec.). Anal. Calcd. for $C_{19}H_{21}DSO_3$: C, 68.85; H, 6.69. Found: C, 68.46; H, 6.56.

Trans-2-(3-chlorophenyl) cyclohexyl p-toluenesulfonate,* m.p. 114°C. Anal. Calcd. for $C_{19}H_{21}SO_3Cl$: C, 62.54; H, 5.80. Found: C, 62.15; H, 6.23.

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*Prepared by D. K. Wedegaertner.

Trans-2-(4-methoxyphenyl) cyclohexyl-p-toluenesulfonate, m.p. 120°C. Anal. Calcd. for $C_{20}H_{24}SO_4$: C, 66.64; H, 6.71. Found: C, 66.00; H, 6.50.

Trans-2-(3-trifluoromethylphenyl) cyclohexyl p-toluenesulfonate, m.p. 94°C. Anal. Calcd. for $C_{20}H_{21}SO_3F_3$: C, 60.29; H, 5.31. Found: C, 60.31; H, 5.67

Trans-2-deutero-2-(3-trifluoromethylphenyl) cyclohexyl p-toluenesulfonate, m.p. 94°C. Anal. Calcd. for $C_{20}H_{20}DSO_3F_3$: C, 60.14; H, 5.55 Found: C, 60.49; H, 5.55

Trans-2-(4-trifluoromethylphenyl) cyclohexyl p-toluenesulfonate,* m.p. 149°C. (dec.). Anal. Calcd. for $C_{20}H_{21}SO_3F_3$: C, 60.29; H, 5.31. Found: C, 60.53; H, 5.47.

Trans-5-t-butyl-2-phenylcyclohexyl p-toluenesulfonate, m.p. 124°C. Anal. Calcd. for $C_{23}H_{30}SO_3$: C, 71.46; H, 7.56. Found: C, 71.58; H, 7.82.

Trans-5-t-butyl-2-deutero-2-phenylcyclohexyl p-toluenesulfonate, m.p. 124°C. Anal. Calcd. for $C_{23}H_{29}DSO_3$: C, 71.28; H, 7.80. Found: C, 71.13; H, 7.72.

3-Bromocyclohexene 3-Bromocyclohexene was prepared by the action of N-bromosuccinimide on cyclohexene. An equimolar (0.5 mole) mixture of cyclohexene and N-bromosuccinimide in 500 ml. of freshly distilled carbon tetrachloride was heated on a steam bath for 2 hours. The reaction mixture was cooled and filtered. The solvent was removed by

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*Prepared by D. K. Wedegaertner.

distillation and the olefin was vacuum distilled.

3-Bromocyclohexene, yield 85% b.p. 35°C. (3.4 mm.). (lit. 141 b.p. 60-63°C. (12 mm.)).

3-Phenylcyclohexene 3-Phenylcyclohexene was prepared by the action of phenyl Grignard reagent on 3-bromocyclohexene. Under Grignard conditions, a 0.5 molar phenyl magnesium bromide solution was produced by the addition of a bromobenzene-ether solution to magnesium turnings. After refluxing the reaction for one hour, an equimolar amount of 3-bromocyclohexene in ether was added slowly. The mixture refluxed 4 hours before the Grignard condensation product was hydrolysed with cold 10 per cent hydrochloric acid. After the hydrolysate was extracted with ether, the extracts were washed with water and dried over magnesium sulfate. The ether was removed by distillation and the product vacuum distilled.

3-Phenylcyclohexene, yield 75%, b.p. 106°C. (14 mm.) (lit. 141 b.p. 76-79°C. (2 mm.)).

4-t-Butylcyclohexanone 4-t-Butylcyclohexanone was prepared by the oxidation of 4-t-butylcyclohexanol (Matheson, Coleman and Bell) with sodium dichromate. A 300 ml. aqueous solution of 0.1 moles of sodium dichromate dihydrate and 0.4 moles of sulfuric acid was added dropwise to 0.3 moles of 4-t-butylcyclohexanol. The reaction was stirred for 24 hours before it was extracted with ether. The extracts were washed with water and dried over magnesium sulfate. A white solid was obtained upon the removal of the ether by a

Rotovac.

4-t-Butylcyclohexanone, m.p. 43°C. (lit. 102 m.p. 47.5-48.5°C.).

Procedures and equipment

Measurement of reaction rates

Base catalyzed elimination reactions of trans-2-arylcyclohexyl p-toluenesulfonate Approximately 0.3 millimoles of a dry p-toluenesulfonate was accurately weighed into a 15 x 125 mm. Pyrex culture tube. Care was taken to prevent the adherence of p-toluenesulfonate crystals to the walls of the upper 50 per cent of the tube. Five milliliters of potassium t-butoxide in t-butanol at 30°C. was pipetted into the sample tube. The tubes were stoppered to keep out moisture and frozen in an ice bath. They were sealed immediately with extreme care to obtain a good round seal on the tube without melting the frozen t-butanol solution. The tubes were placed in the constant temperature bath and periodically shaken until all of the p-toluenesulfonate was dissolved. Ampoules were removed at appropriate intervals and frozen in an ice bath. After the tube was washed with acetone, 95 per cent ethanol and water, it was broken on the sealed end by hitting the tube on the bottom of a thick titration flask. The reaction materials were quantitatively transferred with 100 ml. of distilled water and the excess base was titrated with standard hydrochloric acid using phenolphthalein as the

indicator.

All rates were calculated using the integrated form of the second order rate Equation (13). Rates were calculated by taking the average of the individual rates calculated from each point. Infinity points were taken at approximately ten half lives. Calculated infinity points were based on the amount of p-toluenesulfonate and the amount of base in the tube including the correction for the base being removed by a reaction with glass.

Base catalyzed elimination reactions of 2-phenylethyl p-toluenesulfonate Approximately 0.83 grams of 2-phenylethyl p-toluenesulfonate was weighed accurately into a clean dry 50 ml. volumetric flask. The flask was placed into the constant temperature bath. After 15 minutes for temperature equilibration, the flask was filled to the calibration mark with potassium t-butoxide-t-butanol solution which had also been equilibrated at 30°C. The reaction mixture was shaken until it was homogeneous. At appropriate time intervals 5 ml. aliquots were removed with an automatic pipet and quenched in 50 ml. of distilled water. The excess base was titrated to the phenolphthalein end point with standard hydrochloric acid. Infinity points were taken and checked well with calculated values. Calculations were based on the second order rate equation.

Base reaction with glass It was found that potassium t-butoxide reacted with glass at a detectable rate

when the 15 x 125 Pyrex tubes were used at 102°C. The procedure employed was that used in rate measurements of 2-arylcyclohexyl p-toluenesulfonates with the omission of the p-toluenesulfonate. All measurements were made in duplicate. The results were graphed as ml. of hydrochloric acid used versus time. This was used as a correction for the initial base concentration for each kinetic tube in the 2-arylcyclohexyl p-toluenesulfonate series.

Solvolysis of 2-arylcyclohexyl p-toluenesulfonates

A. Ionic strength equal to 0.1 Approximately 0.3 millimoles of the p-toluenesulfonate were weighed accurately into a 15 x 125 mm. Pyrex culture tube. Care was taken to prevent the crystals from sticking to the tube walls. Lithium perchlorate (0.05 g., 0.1 molar) was weighed quantitatively into the tube. Five milliliters of purified t-butanol at 30°C. was pipeted into the sample. The tubes were quickly frozen and sealed. They were placed in the constant temperature bath and occasionally shaken until the reaction solution was homogeneous. When an ampoule was removed from the oil bath, it was first frozen in an ice bath before the oil was removed by successive washings of acetone, 95 per cent ethanol and finally distilled water. The tube was broken very cautiously in the titration flask by tapping the sealed end on the bottom of the thick wall flask. The reaction produced copious amount of isobutylene and when the ampoules were broken a mild explosion occurred due to the internal gas

gas pressure. The reaction solution was quantitatively transferred to the titration flask with 100 ml. distilled water. The p-toluenesulfonic acid produced was titrated to the phenolphthalein end point with standard sodium hydroxide.

B. Ionic strength equal to 0.0 Procedure used was essentially the same except the lithium perchlorate was not added to the reaction mixture.

Solvolysis rates were calculated based on the integrated form of the first order rate law (Equation 14). Individual rates are calculated from each point.

Substitution reaction of 2-(4-trifluoromethylphenyl) cyclohexene

A. Rate followed by titration of the loss of base The olefin (0.6400 g.) was weighed accurately into a 50 ml. volumetric flask. The flask was equilibrated at 30°C. and filled to the calibration mark with potassium t-butoxide in t-butanol which had been equilibrated at 30°C. Five milliliters of the reaction solution at 30°C. was pipeted into the 15 x 125 mm. Pyrex culture tubes and they were frozen, sealed and placed in the constant temperature bath. The ampoules were removed from the bath, cleaned and broken in the previously described manner and titrated with standard acid to the phenolphthalein end point.

B. Rate followed by the titration of appearance of fluoride ion The olefin-base samples were prepared, run, broken and titrated in the manner described above. The

neutral solution was then titrated with standard thorium nitrate solution after 4.5 ml. of buffer and 15 drops of Alizarin Red S. indicator were added (142). Both A and B were calculated using second order kinetic equations.

C. Semiquantitative test for the fluoride ion at the infinity points of the reaction between 2-(4-trifluoromethylphenyl) cyclohexyl p-toluenesulfonate and potassium t-butoxide The procedure used in B was followed.

Isomerization of olefins

Isomerization of 3-phenylcyclohexene to 1-phenylcyclohexene Two samples of each olefin of approximately 0.1 molar were weighed accurately into 15 x 125 mm. culture tubes. After each sample had been dissolved in 5 ml. of potassium t-butoxide-t-butanol solution, one tube of each olefin was frozen, sealed and placed in the constant temperature bath. The other two samples were stoppered and kept at room temperature for the same time interval. The ampoules were removed from the oil bath and cleaned with acetone, 95 per cent ethanol and water before being broken in a thick walled conical flask. All of the samples were quantitatively transferred to 50 ml. volumetric flasks and diluted to the calibration mark with 95 per cent ethanol. Further dilutions were made with 95 per cent ethanol before the ultraviolet spectra of the olefins were measured on a Beckman DK2a recording spectrophotometer.

Purification of materials

Anhydrous tert-butanol Purification procedure was described on page 114.

Potassium t-butoxide The method of preparing approximately 0.1M. potassium t-butoxide was described on page 115.

Standardization of 0.1N hydrochloric acid The approximately 0.1N hydrochloric acid was standardized by J. Beckman against primary standard sodium carbonate using the methyl red procedure (136).

Standardization of 0.02N sodium hydroxide Sodium hydroxide (0.02074N) was standardized against primary standard potassium acid phthalate. (Bakers Analytical Reagent). The primary standard was finely ground and dried at 110°C. for 24 hours. Carbonate free base was prepared by making a 50 per cent solution of sodium hydroxide and letting the carbonate settle out. The normality of the base is an average of three determinations with a relative precision less than one part per thousand. The base normality was cross-checked with the acid normality with a relative error of approximately one part per thousand. The sodium hydroxide solution was stored in a Polyethylene bottle protected by a magnesium perchlorate-ascarite drying tube.

Standard thorium nitrate solution Thorium nitrate tetrahydrate (4.5 g.) was dissolved in a liter of distilled water. This solution was standardized against

analytical reagent grade sodium fluoride which had been dried for two hours at 110°C. Approximately 0.1 g. sodium fluoride was accurately weighed into an conical flask and dissolved in 45 ml. of distilled water. After 4 ml. of the monochloroacetic acid buffer and 5 drops of Alizarin red S indicator were added, the solution was titrated to a definite red color using a 10 ml. buret.

Monochloroacetic acid buffer Monochloroacetic acid (94.5 g.) and 30.0 g. of sodium hydroxide were dissolved in distilled water and diluted to one liter.

Alizarin red S indicator Fifty milligrams of Hartman and Leddon alizarin red S was dissolved in 25 ml. of distilled water.

Kinetic data

The rates of the base-promoted elimination reactions of the 2-arylcyclohexyl p-toluenesulfonates are reported in Tables 82 through 94. The volumes of titrant reported in the second column of each table are the amounts of hydrochloric acid required to neutralize five milliliter aliquots of the reaction mixture. The third column is the initial base concentration corrected for the loss of base with time because of the reaction with glass (Figure 12). The fourth column is the millimoles of p-toluenesulfonate weighed into the ampoules. Also included are the normality of the titrant, initial concentrations of p-toluenesulfonates and base, the

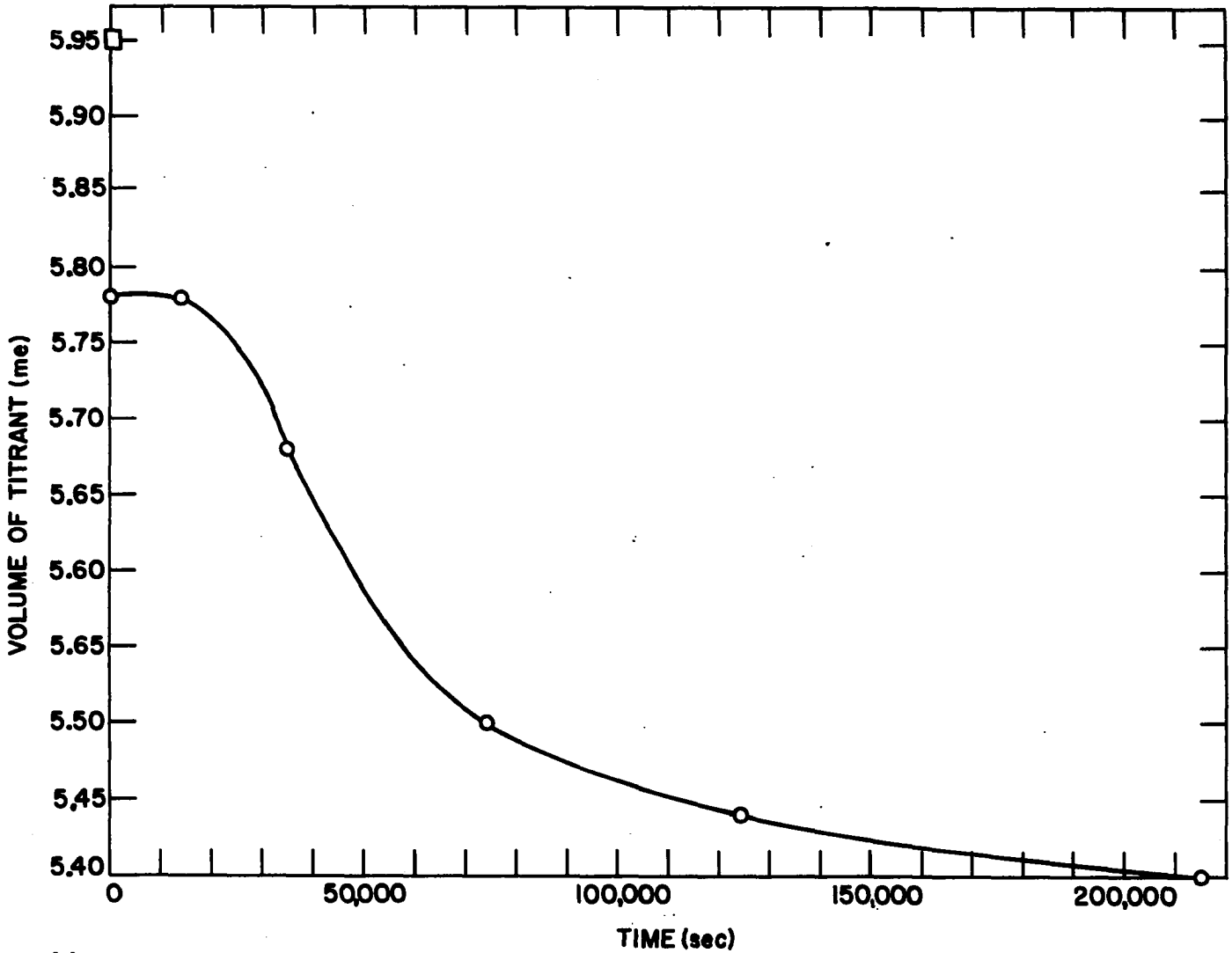

Figure 11. Reaction of potassium t-butoxide-t-butanol solution with Pyrex glass at 102°C.

second order rate constants calculated for each point and the average rate constant. All rates were corrected by a factor determined by the rates of β-phenylethyl p-toluenesulfonates in the corresponding bases. Kinetics determined in base 1 are corrected by a factor of 2.66:2.44 which is the ratio of rates of β-phenylethyl p-toluenesulfonate in base 2a:base 1. Rates are not corrected for volume expansion from 30° to 102°C. The base was equilibrated at 30°C. before 5 ml. aliquots were added to the samples. Kinetic determinations concerning β-phenylethyl have been discussed previously.

Table 78. The reaction of potassium t-butoxide-t-butanol solution with Pyrex glass (15 x 125 mm. culture tubes) at 102°C.

Time (sec.)	Volume of titrant[a] (ml.)
0	5.78
13,900	5.78
34,800	5.68
74,000	5.50
124,000	5.44
215,600	5.40

[a] N_{HCl} = 0.1005 n; concentration of base = 5.95 ml. of titrant.

Table 79. Rate of reaction of 2-phenylethyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 30°C. for base solution number 1

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^3$ (liter $mole^{-1}$ $sec.^{-1}$)
0	6.90	--
493	6.50	2.46
1,111	6.11	2.42
1,606	5.85	2.44
2,543	5.47	2.45
Rate over entire period		2.44 ± 0.01

[a] N_{HCl} = 0.1005; conc. of p-toluenesulfonate = 0.0541 M; conc. of base = 0.1387 M.

Table 80. Rate of reaction of 2-phenylethyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution at 30°C. for base solution number 2a.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^{-3}$ (liter $mole^{-1}$ $sec.^{-1}$)
0	5.73	--
532	5.34	2.69
1,347	4.90	2.61
2,309	4.48	2.69
Rate over entire period		2.66 ± 0.04

[a] N_{HCl} = 0.1005; conc. of p-toluenesulfonate = 0.0592 M; conc. of base = 0.1152 M.

Table 81. Rate of reaction of 2-phenylethyl p-toluenesulfonate potassium t-butoxide-t-butanol solution at 30°C. for base solution number 2b.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^3$ (liter mole^{-1} sec.$^{-1}$)
0	5.74	--
472	5.38	2.39
1,053	5.04	2.30
1,740	4.70	2.31
2,712	4.35	2.27
4,202	3.96	2.23
5,584	3.69	2.24
Rate over entire period		2.29 ± 0.04

[a] N_{HCl} = 0.1005, conc. of p-toluenesulfonate = 0.0610 M.; conc. of base = 0.1154 M.

Table 82. Rate of reaction of trans-2-phenylcyclohexyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution number 1 at 102°C.

Time elapsed (sec.)	Volume of Titrant[a] (ml.)	a (m. moles)	b (m. moles)	$k_2 \times 10^4$ (liter mole^{-1} sec.$^{-1}$)
15,000	6.33	0.7075	0.2633	1.57[b]
26,400	5.96	0.7050	0.3541	1.04
52,800	5.78	0.6985	0.2315	1.06
61,000	5.36	0.6965	0.2923	1.05
73,000	5.08	0.6940	0.3102	1.05
83,400	5.39	0.6934	0.2318	1.06
106,800	4.73	0.6919	0.3090	1.02
142,200	4.40	0.6904	0.3568	1.00
Average rate over 7 points[b]				1.04 ± 0.02
Rate corrected for kinetic standard base 2a				1.13 ± 0.02

[a] $N_{HCl} = 0.1005$.

[b] Point not used in average rate.

[c] Calculated infinity point = 4.43 ml.

Table 83. Rate of reaction of trans-2-phenylcyclohexyl p-toluenesulfonate in potassium-t-butoxide-t-butanol solution number 2a at 102°C.

Time elapsed (sec.)	Volume of Titrant[a] (ml.)	a	b	$k_2 \times 10^4$ (liter mole^{-1} sec.$^{-1}$)
11,872	5.33	0.5809	0.3577	1.02[b]
21,802	4.96	0.5794	0.3468	1.13
30,084	4.63	0.5774	0.3668	1.18
39,115	4.72	0.5749	0.2581	1.22
48,881	4.45	0.5728	0.2890	1.16
57,697	4.41	0.5703	0.2609	1.16
83,637	3.84	0.5668	0.3199	1 09
103,900	3.64	0.5653	0.3184	1.07
Infinity point[c]	2.74	0.5507	0.2760	
Average rate over 7 points[b]				1.15 ± 0.04
Rate corr. for kinetic standard base 2a				1.15 ± 0.04

[a] N_{HCl} = 0.1005.

[b] Point not used in average rate.

[c] Calculated infinity point = 2.73 ml.

Table 84. Rate of reaction of *trans*-2-phenylcyclohexyl-*p*-toluenesulfonate in potassium-*t*-butoxide-*t*-butanol solution number 2b at 102°C.

Time elapsed (sec.)	Volume of Titrant[a] (ml.)	a (m. moles)	b (m. moles)	$k_2 \times 10^4$ (liter mole^{-1} sec.$^{-1}$)
9,838	5.38	0.5759	0.3632	0.93
19,667	5.08	0.5749	0.3380	1.00
30,788	4.88	0.5718	0.2811	1.05
45,906	4.35	0.5683	0.3532	1.02
69,498	3.84	0.5628	0.3601	1.06
85,980	3.88	0.5613	0.2984	1.08
104,894	3.85	0.5603	0.3011	0.90
134,898	3.10	0.5598	0.3607	1.05
163,552	2.82	0.5578	0.3650	1.14
Average rate of 9 points				1.02 ± 0.06
Rate corr. for kinetic standard base 2b				1.18 ± 0.06

[a] $N_{HCl} = 0.1005$.

Table 85. Rate of reaction of trans-2-deutero-2-phenylcyclohexyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution number 1 at 102°C.

Time elapsed (sec.)	Volume of Titrant[a] (ml.)	a (m. moles)	b (m. moles)	$k_2 \times 10^4$ (liter mole^{-1} sec.$^{-1}$)
15,000	6.41	0.7075	0.2999	1.17[b]
26,400	5.92	0.7050	0.3784	1.01[b]
52,800	5.44	0.6985	0.3268	0.97[b]
61,000	5.68	0.6965	0.2507	0.91
73,000	5.31	0.6940	0.2987	0.88
83,400	5.22	0.6934	0.2957	0.86
106,800	5.08	0.6919	0.2740	0.88
142,200	4.82	0.6904	0.2755	0.87
Infinity point[c]	3.93	0.6774	0.2842	
Average rate of 5 points[b]				0.88 ± 0.02
Rate corr. for kinetic standard base 2a				0.96 ± 0.02

[a] $N_{HCl} = 0.1005$.

[b] Points not used in average rate.

[c] Calculated infinity point = 3.91 ml.

Table 86. Rate of reaction of *trans*-2-deutero-2-phenylcyclohexyl *p*-toluenesulfonate in potassium *t*-butoxide-*t*-butanol solution number 2a at 102°C.

Time elapsed (sec.)	Volume of Titrant[a] (ml.)	a (m. moles)	b (m. moles)	$k_2 \times 10^4$ (liter mole^{-1} sec.$^{-1}$)
11,944	5.30	0.5809	0.3533	1.11[b]
21,887	5.08	0.5794	0.3114	1.05
30,154	4.79	0.5774	0.3479	1.02
39,185	4.69	0.5749	0.3029	1.03
48,806	4.42	0.5728	0.3376	0.98
57,765	4.22	0.5703	0.3415	0.99
83,742	3.46	0.5668	0.4360	0.96
104,042	3.84	0.5653	0.3038	0.94
Infinity point[c]	2.36	0.5507	0.3141	
Average rate of 7 points[b]				1.00 ± 0.03
Rate corr. for kinetic standard base 2a				1.00 ± 0.03

[a] $N_{HCl} = 0.1005$.

[b] Point not used in average rate.

[c] Calculated infinity point = 2.35 ml.

Table 87. Rate of reaction of trans-2-(3-chlorophenyl) cyclohexyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution number 1 at 102°C.

Time elapsed (sec.)	Volume of Titrant[a] (ml.)	a (m. moles)	b (m. moles)	$k_2 \times 10^4$ (liter $mole^{-1}$ $sec.^{-1}$)
11,150	5.90	0.7075	0.2664	3.92
16,250	5.44	0.7075	0.3319	3.32
27,750	4.75	0.7045	0.4059	2.60
37,250	5.23	0.7020	0.2779	2.27
50,150	4.67	0.6990	0.3275	2.18
75,050	3.92	0.6934	0.4037	1.81
Average rate				--

[a] $N_{HCl} = 0.1005$.

Table 88. Rate of reaction of trans-2-(3-chlorophenyl) cyclohexyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution number 2a at 102°C.

Time elapsed (sec.)	Volume of Titrant[a] (ml.)	a (m. moles)	b (m. moles)	$k_2 \times 10^4$ (liter mole^{-1} sec.$^{-1}$)
4,412	5.44	0.5814	0.2771	2.69[b]
7,850	5.22	0.5809	0.3190	2.24[b]
11,380	5.17	0.5809	0.2743	2.03
18,632	4.94	0.5804	0.2639	1.92
27,676	4.68	0.5779	0.2631	1.84
40,612	4.08	0.5749	0.3311	1.77
54,305	4.18	0.5713	0.2532	1.74
83,058	3.46	0.5668	0.3113	1.72
Infinity point[c]	2.85	0.5507	0.2480	
Average rate of 6 points[b]				1.84 ± 0.09
Rate corr. for kinetic standard base 2a				1.84 ± 0.09

[a] N_{HCl} = 0.1005.

[b] Points not used in average rate.

[c] Calculated infinity point = 3.01 ml.

Table 89. Rate of reaction of trans-2-(4-methoxyphenyl) cyclohexyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution number 2b at 102°C.

Time elapsed (sec.)	Volume of Titrant[a] (ml.)	a (m. moles)	b (m. moles)	$k_2 \times 10^4$ (liter mole^{-1} sec.$^{-1}$)
9,348	5.21	0.5759	0.3057	1.83
19,159	4.71	0.5749	0.3459	1.75
30,280	4.52	0.5718	0.2907	1.69
38,240	4.05	0.5703	0.3559	1.69
45,431	3.94	0.5683	0.3376	1.68
68,968	3.61	0.5628	0.3057	1.76
80,243	3.31	0.5618	0.3343	1.73
104,400	3.13	0.5603	0.3124	1.87
134,397	2.74	0.5598	0.3362	1.93
Average rate of 9 points				1.77 ± 0.07
Rate corr. for kinetic standard base 2a				2.06 ± 0.07

[a] $N_{HCl} = 0.1005$.

Table 90. Rate of reaction of 5-t-butyl-2-phenylcyclohexyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution 2b at 102°C.

Time elapsed (sec.)	Volume of Titrant[a] (ml.)	a (m. moles)	b (m. moles)	$k_2 \times 10^4$ (liter $mole^{-1}$ $sec.^{-1}$)
9,223	5.47	0.5759	0.3001	0.92[b]
18,914	5.25	0.5749	0 2949	0.84[b]
30,040	5.08	0.5718	0.3084	0.68
45,187	4.85	0.5683	0.3130	0.63
68,720	4.53	0.5628	0.3164	0.60
134,160	4.28	0.5598	0.2794	0.60
251,338	3.68	0.5543	0.2791	0.49
332,929	3.12	0.5507	0.3304	0.49
424,394	3.19	0.5467	0.2745	0.51
Average rate for 7 points[b]				0.57 ± 0.06
Rate corr. for kinetic standard base 2a				0.66 ± 0.06

[a] N_{HCl} = 0.1005.

[b] Points not used in average rate.

Table 91. Rate of reaction of trans-5-t-butyl-2-deutero-2-phenylcyclohexyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution 2a at 102°C.

Time elapsed (sec.)	Volume of Titrant[a] (ml.)	a (m. moles)	b (m. moles)	$k_2 \times 10^4$ (liter $mole^{-1}$ $sec.^{-1}$)
8,860	5.57	0.5759	0.3303	0.50[b]
18,751	5.46	0.5749	0.2833	0.46[b]
29,858	5.25	0.5718	0.3306	0.44[b]
44,991	5.17	0.5683	0.2854	0.38
68,534	4.92	0.5628	0.2872	0.38
133,973	4 34	0.5598	0.3275	0.36
251,083	4.01	0.5543	0.2846	0.32
332,767	3.61	0.5507	0.2921	0.36
424,242	3.27	0.5467	0.3066	0.37
Average rate for 6 points[b]				0.36 ± 0.01
Rate corr. for kinetic standard base 2a				0.36 ± 0.01

[a] $N_{HCl} = 0.1005$.

[b] Points not used in average rate.

Table 92. Rate of reaction of trans-2-(3-trifluoromethylphenyl) cyclohexyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution 2a at 102°C.

Time elapsed (sec.)	Volume of Titrant[a] (ml.)	a (m. moles)	b (m. moles)	$k_2 \times 10^4$ (liter $mole^{-1}$ $sec.^{-1}$)
4,288	5.50	0.5814	0.2946	2.10
7,676	5.32	0.5809	0.2829	2.08
11,204	5.14	0.5809	0.2936	2.02
18,430	4.90	0.5804	0.2673	2.03
25,157	4.51	0.5779	0.3110	2.00
38,268	4.08	0.5749	0.3205	1.98
54,036	4.03	0.5713	0.2635	1.96
82,979	3.51	0.5668	0.2879	1.91
Infinity point[b]	2.30	0.5507	0.2944	
Average rate for 8 points				2.01 ± 0.05
Rate corr. for kinetic stand base 2a				2.01 ± 0.05

[a] $N_{HCl} = 0.1005$.

[b] Calculated infinity point = 2.55 ml.

Table 93. Rate of reaction of trans-2-deutero-2-(3-trifluoromethylphenyl) cyclohexyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution 2a at 102°C.

Time elapsed (sec.)	Volume of Titrant[a] (ml.)	a (m. moles)	b (m. moles)	$k_2 \times 10^4$ (liter mole^{-1} sec.$^{-1}$)
4,371	5.64	0.5814	0.2754	1.08
7,734	5.52	0.5809	0.2919	1.07
11,275	5.46	0.5809	0.2629	1.02
18,481	5.17	0.5804	0.2879	1.07
23,385	4.93	0.5779	0.2874	1.12
47,702	4.55	0.5749	0.2912	1.06
83,005	4.08	0.5713	0.2824	1.07
103,119	3.98	0.5668	0.2576	1.09
Infinity point[b]	2.57	0.5507	0.2696	
Average rate for 8 points				1.08 ± 0.03
Rate corr. for kinetic standard base 2a				1.08 ± 0.03

[a] $N_{HCl} = 0.1005$.

[b] Calculated infinity point = 2.80 ml.

Table 94. Rate of reaction of trans-2-(4-trifluoromethylphenyl) cyclohexyl p-toluenesulfonate in potassium t-butoxide-t-butanol solution 2a at 102°C.

Time elapsed (sec.)	Volume of Titrant[a] (ml.)	a (m. moles)	b (m. moles)	$k_2 \times 10^4$ (liter mole^{-1} sec.$^{-1}$)
3,939	5.34	0.5814	0.2357	4.78
7,312	4.96	0.5809	0.2332	5.57
10,848	4.56	0.5809	0.2492	6.12
13,502	4.36	0.5809	0.2435	6.59
18,091	3.77	0.5804	0.2803	7.76
23,138	3.56	0.5789	0.2568	10.01
82,321	1.21	0.5668	0.2977	b
Average rate				--

[a] $N_{HCl} = 0.1005$.

[b] 150 per cent of reaction was complete at this point based on what was expected for a simple second order elimination reaction.

Table 95. Rate of reaction of trans-2-(4-trifluoromethylphenyl) cyclohexene in potassium t-butoxide-t-butanol solution 2b at 102°C. followed by an acid titration

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^4$ (liter $mole^{-1}$ $sec.^{-1}$)
0	5.38	--
1,007	5.25	5.30
1,890	5.21	3.70
3,730	5.07	3.51
8,253	4.69	4.00
11,468	4.51	3.89
29,134	3.57	5.07
36,914	3.23	6.64
Average rate		--

[a] N_{HCl} = 0.1005, conc. of olefin = 0.0495 M.; conc. of base = 0.1081 M.

Table 96. Rate of reaction of trans-2-(4-trifluoromethylphenyl) cyclohexene in potassium t-butoxide-t-butanol solution 2b at 102°C. followed by a fluoride titration

Time elapsed (sec.)	Volume of titrant[a] (ml.)	$k_2 \times 10^4$ (liter mole^{-1} sec.$^{-1}$)
0	0.48	--
1,007	0.65	2.58
1,890	0.76	2.29
3,730	0.93	1.91
8,253	1.50	2.11
11,468	1.90	2.24
29,134	3.49	2.79
36,914	4.03	2.96
Average rate		--

[a] 7.68×10^{-4} grams of fluoride ion per ml. of thorium ion; conc. of olefin = 6.02 ml. of Th^{-4}; conc. of base = 12.73 ml. of Th^{-4}.

Table 97. Rate of reaction of trans-2-phenylcyclohexyl p-toluenesulfonate in t-butanol with lithium perchlorate at 102°C.

Time Elapsed (sec.)	p-toluenesulfonate (molar) x 10^3	lithium perchlorate (molar)	Volume of titrant[a] (ml.)	k_1 x 10^5 ($sec.^{-1}$)
18,360	5.066	0.0934	3.50	1.84
29,640	4.666	0.0940	5.00	1.98
36,900	5.417	0.0953	5.25	1.39
105,720	5.096	0.0938	11.27	2.37
Average rate				--

[a] N_{HCl} = 0.02074; blank = 0.30 ml.

Table 98. Rate of reaction of trans-2-(4-methoxyphenyl) cyclohexyl p-toluenesulfonate in t-butanol with lithium perchlorate at 102°C.

Time Elapsed (sec.)	p-toluenesulfonate (molar) x 10^3	lithium perchlorate (molar)	Volume of titrant[a] (ml.)	k_1 x 10^5 ($sec.^{-1}$)
18,360	4.267	0.0947	9.80	1.66
29,640	4.333	0.0944	10.45	--
36,900	4.772	0.0932	11.10	--
105,720	4.405	0.0944	10.60	--

[a] H_{NaOH} = 0.02074; blank = 0.30 ml.

Table 99. Rate of reaction of trans-5-t-butyl-2-phenylcyclohexyl p-toluenesulfonate in t-butanol with lithium perchlorate at 102°C.

Time Elapsed (sec.)	p-toluenesulfonate (molar) x 10^3	lithium perchlorate (molar)	Volume of titrant[a] (ml.)	k_1 x 10^5 ($sec.^{-1}$)
29,760	4.776	0.0934	5.00	1.92
36,960	4.703	0.0930	6.55	2.33
105,780	4.698	0.0936	10.40	2.26
Average rate				--

[a] N_{NaOH} = 0.02074; blank = 0.30 ml.

Table 100. Rate of reaction of trans-2-phenylcyclohexyl p-toluenesulfonate in t-butanol at 102°C.

Time elapsed (sec.)	p-toluenesulfonate (molar)	Volume of titrant[a] (ml.)	k_1 x 10^6 ($sec.^{-1}$)
10,560	4.382	0.20	1.85 ± 10^{-6}
81,120	4.400	1.92	2.46 ± 10^{-6}

[a] N_{NaOH} = 0.02074; blank = 0.23 ml.

Table 101. Rate of reaction of trans-2-(4-methoxyphenyl) cyclohexyl p-toluenesulfonate in t-butanol at 102°C.

Time elapsed (sec.)	p-toluenesulfonate (molar)	Volume of titrant[a] (ml.)	$k_1 \times 10^6$ ($sec.^{-1}$)
10,800	4.344	0.56	5.12
81,420	4.405	5.31	8.52

[a] N_{NaOH} = 0.02074; blank = 0.23 ml.

Table 102. Rate of reaction of trans-5-t-butyl-2-phenyl-cyclohexyl p-toluenesulfonate in t-butanol at 102°C.

Time elapsed (sec.)	p-toluenesulfonate (molar)	Volume of titrant[a] (ml.)	$k_1 \times 10^6$ ($sec.^{-1}$)
10,860	4.403	0.44	3.86
81,480	4,346	2.29	3.02

[a] N_{NaOH} = 0.02074; blank = 0.23 ml.

Table 103. Isomerizations of 3-phenylcyclohexene to 1-phenylcyclohexene in potassium t-butoxide-t-butanol at 102°C.

Olefin	Time Elapsed (hours)	Conc. of olefin (molar 10^2)	Absorbance	Extinction Coeff.
1-phenyl	0	1.263	1.481[a]	11,730
	11	1.248	1.475[a]	at 246 mμ.
3-phenyl	0	1.331	1.319[b]	991
	11	1.350	0.712[a]	at 243 mμ.

[a]Absorbance after 1:100 dilution.

[b]Absorbance after 1:10 dilution.

Part V: Beta Elimination Studies of Cis and Trans-2-Carbethoxycyclopentyl p-toluenesulfonates

Preparation and purification of materials

Preparation of 2-carbethoxycyclopentyl compounds

Cis and trans-2-carbethoxycyclopentanols The 2-carbethoxycyclopentanols were prepared by the reduction of 2-carbethoxycyclopentanone with sodium borohydride. The sodium borchydride (0.05 mole) was stirred slowly into a cold solution of 60 ml. of absolute ethanol and ketone (0.1 mole). The reaction was warmed to room temperature and stirred for one hour. The ethanol was removed by vacuum on a Rotovac. The residue was acidified with 10 per cent hydrochloric acid and extracted with ether. After washing and drying the extracts, the ether was removed and the alcohols separated by vacuum distillation on a spinning band column. Good yields of both alcohols were attained.

Cis-2-Carbethoxycyclopentanol, b.p. 60°C. (0.3 mm.).

Trans-2-Carbethoxycylopentanol, b.p. 70°C. (0.3 mm.).

Anal. Calcd, for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 59.43; H, 8.94.*

Infrared dilution studies of the alcohols showed intramolecular hydrogen bonding in the hydroxyl region for the

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*Carbon analysis is believed to be in error because the analysis of cis-2-carbethoxyclopentyl p-toluenesulfonate is good and the preparation of these compounds is the same.

lower boiling alcohol and intermolecular hydrogen bonding for the higher boiling fraction. Structural assignments were made with this evidence.

Gas phase chromatographic analysis showed the alcohols to be greater than 98% pure. Retention times of 14 and 23 minutes for the *cis* and *trans* alcohols respectively on a one meter UCON LB 550X 1:4 on 60/80 Regular Chromosorb W column at 145°C and a helium flow of 30 ml./min. were observed.

Trans-2-carbethoxycyclopentyl *p*-toluenesulfonate

The *trans*-2-carbethoxycyclopentyl *p*-toluenesulfonate was prepared from the corresponding alcohol according to Tipson's 134 procedure. *p*-Toluenesulfonyl chloride (1.8 g., 0.0092 mole) was added to a solution of the alcohol (1 g., 0.0061 mole) and 10 ml. of anhydrous pyridine at 0°C. The mixture was swirled and placed in the refrigerator (5°C.) for 24 hours. During this time pyridine hydrochloride crystals appeared. The mixture was poured into ice water and extracted with ether. After the extracts were washed with 10 per cent hydrochloric acid and water, the ether solution was dried and the ether removed carefully. The remaining oil was crystallized from ether-pentane mixture at -80°C. The re-crystallization procedure was repeated three more times. The last trace of solvent was removed by drying the liquid *in vacuo*.

Trans-2-carbethoxycyclopentyl *p*-toluenesulfonate, yield

40%, m.p. -4°C.

Cis-2-carbethoxycyclopentyl p-toluenesulfonate

The cis-2-carbethoxycyclopentyl p-toluenesulfonate was prepared from the corresponding alcohol by the procedure described above. The procedure differs slightly because the p-toluenesulfonate crystallizes in the ice water. The solid is filtered, washed with 10 per cent hydrochloric acid and water. The product is dissolved in ether and dried over anhydrous magnesium sulfate. The bulk of the ether was removed and the p-toluenesulfonate recrystallized from an ether-benzene mixture. Recrystallization was repeated three more times from absolute ethanol.

Cis-2-carbethoxycyclopentyl p-toluenesulfonate, yield 90%, m.p. 110°C. Anal. Calcd. for $C_{15}H_{20}SO_5$: C, 57.67; H, 6.45; S, 10.27. Found: C, 57.56; H, 6.44; S, 10.30.

Preparation of 1-carbethoxycyclopentene 1-Carbethoxycyclopentene was prepared by the base-promoted elimination of cis-2-carbethoxycyclopentyl p-toluenesulfonate. The p-toluenesulfonate was prepared from 0.083 moles of cis-2-carbethoxycyclopentanol in the usual manner. After the p-toluenesulfonate had been dried, it was dissolved in 100 ml. absolute ethanol and 100 ml. of 1N sodium ethoxide. The mixture was poured into ice water and extracted with ether. After the extracts were dried and the ether removed, the olefin was distilled.

1-carbethoxycyclopentene, yield 75%, b.p. 185°C.

Preparation of 2-deutero-2-carbethoxycyclopentanone

The deuterium exchange was accomplished by two reactions. First, the sodium salt of 2-carbethoxycyclopentanone was prepared by adding deuterium oxide and the ketone to a benzene solution of sodium hydride. (35 g. of 53.5 per cent oil emulsion). Sodium hydride was dissolved in one liter of anhydrous benzene. The ketone (100 g.) was added cautiously. Deuterium oxide (12 ml. of 99 per cent pure) was added dropwise to the reaction mixture. The solid was dissolved by the addition of deuterium chloride made by the slow addition of 8 ml. of deuterium oxide to 112 g. of hot benzoyl chloride. After the solution was filtered and the benzene removed, the ketone was vacuum distilled. Nuclear magnetic resonance spectral analysis showed that the ketone was approximately 50 per cent deuterated. Reduction of the ketone with sodium borohydride in absolute ethanol produced alcohols with no deuterium incorporation.

Procedures and equipment

Measurement of reaction rates

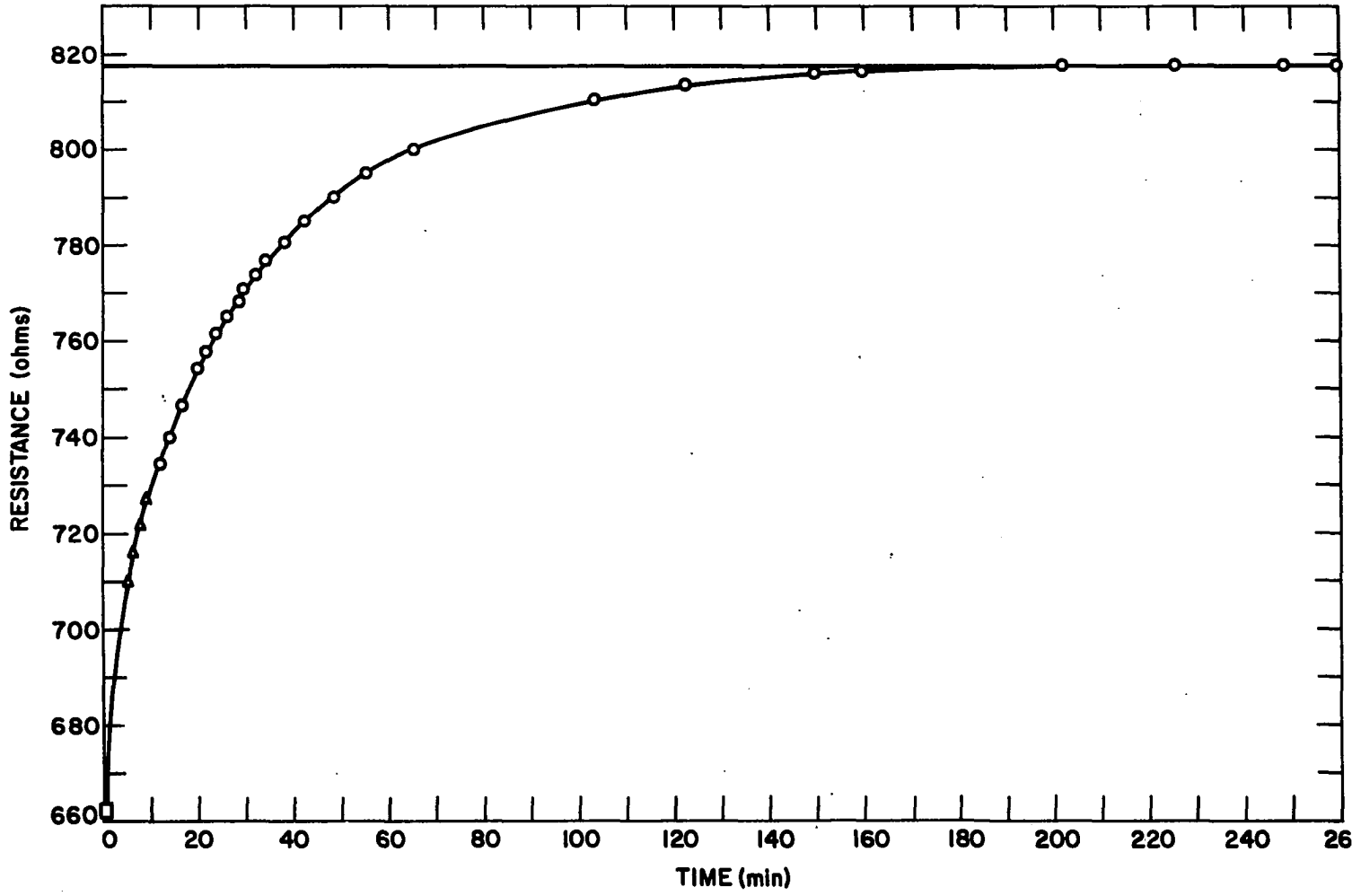
Base catalyzed elimination reactions followed by resistance measurements A solution 0.05 molar in p-toluenesulfonate and 0.1 molar in base was prepared in the following manner. The desired compound (0.005 mole) was weighed accurately into the conductance cell and dissolved

in approximately 90 ml. of absolute ethanol. Heating was required for the dissolution of the cis-2-carbethoxycyclopentyl p-toluenesulfonate. After equilibration at the reaction temperature, this solution was diluted to the calibration mark of the conductance cell with the correct amount of 1M. base and absolute ethanol. Resistance measurements were made at given time intervals until the reaction was complete. This rate data was graphed as resistance versus time (Figure 12). At this time, the conductance cell was removed from the coolant and the excess base in the reaction solution was titrated with standard hydrochloric acid.

Time zero was unknown, but the concentrations of sodium p-toluenesulfonate and sodium ethoxide were known at any per cent reaction. There not being any relationships between resistance and concentration of these substances in ethanol, that would make it possible to relate resistance to per cent of reaction completed, a calibration curve was constructed by calculating the amounts of sodium ethoxide and sodium p-toluenesulfonate corresponding to 0, 25, 50, 75, 100 per cent of reaction and measuring the resistance of these solutions. The organic p-toluenesulfonate did not contribute to the solution's resistance. This assumption was justified by the agreement between experimental and synthetic infinity points.

The resistance of synthetic reaction points was measured in the following manner. A 0.2N sodium ethoxide-ethanol solution was standardized by using a given volume of base at room

Figure 12. Resistance versus time on the kinetic run of trans-2-carbethoxycyclopentyl p-toluenesulfonate and sodium ethoxide-absolute ethanol solution at 0°C.


820
800
780
760
740
720
700
680
660
RESISTANCE (ohms)
0
20
40
60
80
100
120
140
160
180
200
220
240
260
TIME (min)

temperature diluted to the conductance cell's calibration mark at the kinetic reaction's temperature and then titrated with standard acid. The amount of sodium p-toluenesulfonate was accurately weighed into the cell and dissolved in a calculated amount of sodium ethoxide-absolute ethanol solution. Heating was required for solution. The resistance of the synthetic reaction solution was measured in a manner similar to that already described. The results (Figure 13) were graphed as per cent of the reaction's total resistance change versus per cent reaction. This gave an empirical calibration curve where the moles of p-toluenesulfonate reacted were calculated from resistance for any given time.

Individual resistance measurements Each resistance measurement was conducted in the following manner. A 1500 ml. and a 250 ml. Dewar flasks were filled with the proper coolant. The vessels were covered with Styrafoam caps and allowed two hours to come to equilibrium temperature. The stirrer (see Figure 14) was cooled to the proper temperature in a 100 ml. volumetric flask of absolute ethanol using an ice or dry ice-acetone bath. The conductance cell, filled to 95 per cent level, was placed in the coolant for one hour with occasional shaking. At the same time, absolute ethanol and, if needed, 1M. sodium ethoxide were cooled in 10 ml. graduated centrifuge tubes using the smaller Dewar flask. After temperature equilibrium had been established, the calculated volume of base was pipeted quickly into the cell.

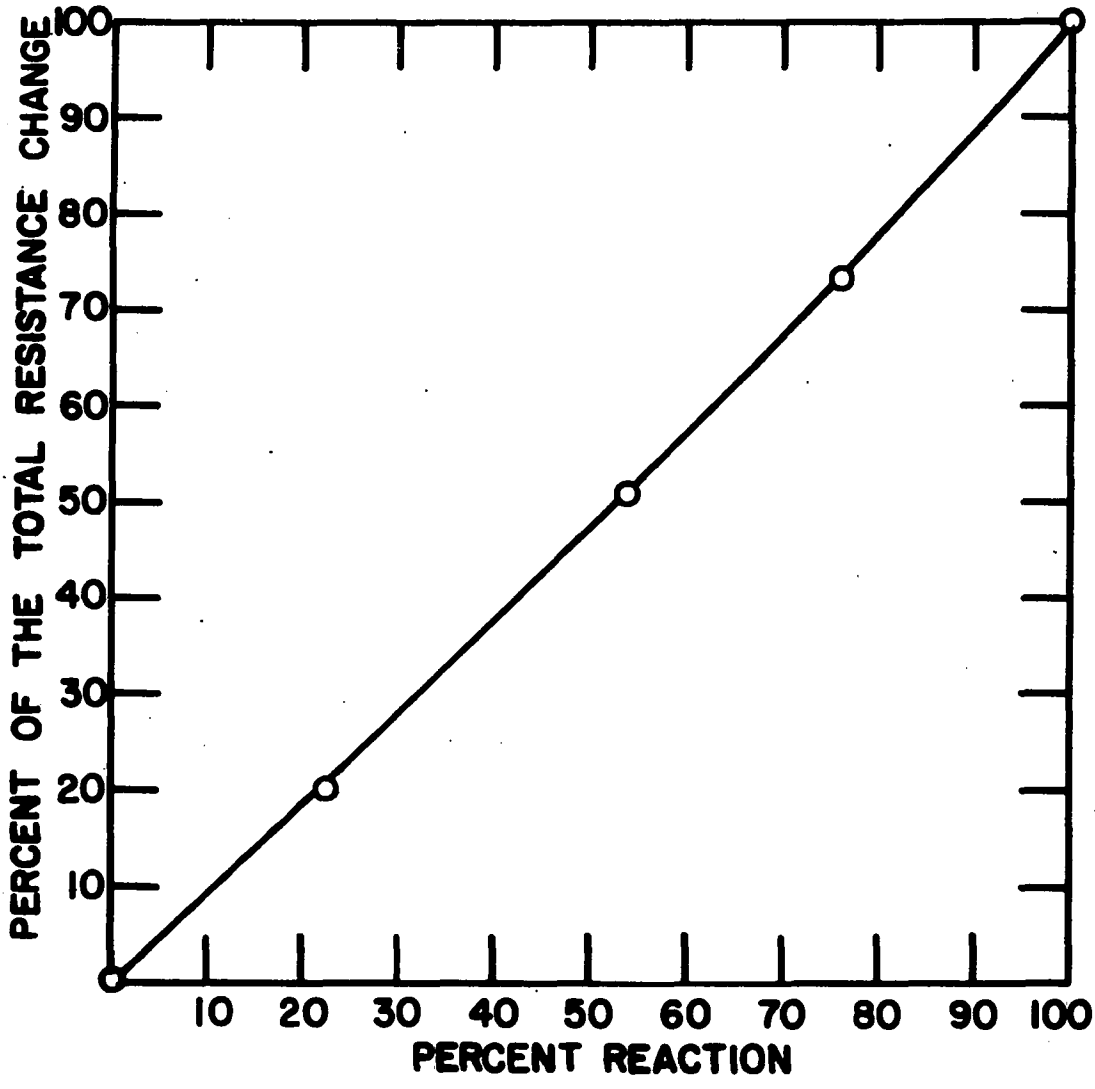


Figure 13. Per cent of total resistance change versus per cent of reaction of 0.01692 molar trans-2-carbethoxycyclopentyl p-toluenesulfonate with 0.02739 molar sodium ethoxide in ethanol at 0°C.

After the cell was filled to the calibration mark with cold absolute ethanol, it was shaken vigorously for 10 seconds and replaced in a coolant. The stirrer was immediately placed into the cell. The solution was stirred for five minutes while the cell leads were attached to the bridge and major resistance and capacitance adjustments were made. Resistance measurements were recorded starting at approximately one minute after the stirrer was turned off.

All rates were second order as evidenced by the constant values obtained when the integrated form of the second order rate equation was applied to the data. Rates were calculated from each point.

Titration procedure The sample of base in the conductance cell was transferred quantitatively to a 600 ml. beaker with small amounts of absolute ethanol. 400 ml. of fresh conductance water was added and the solution titrated immediately with standard acid. The titration was followed with a Photovolt Model 115 Electronic pH Meter using glass-calomel electrode system. (The pH meter was standardized with Bechman pH7 buffer prior to use). The end point was determined graphically. It was found that carbon dioxide and other minute impurities necessitated the use of fresh conductance water.

Product analysis A completely reacted solution of 0.05 molar 2-carbethoxycyclopentyl p-toluenesulfonate and 0.1 molar sodium ethoxide was diluted with a large amount of water

and extracted with ether. The ether extracts were dried and carefully concentrated by removing the ether on a Rotovac. The solution, still containing large amounts of ether, was analyzed on a one meter column of Apiezon L 1:3 on firebrick at 100°C.

Equipment

Jones Bridge The resistance measurements were made with a Jones conductivity bridge (Leeds and Northrup Company, catalog number 4666), designed in accordance with the principles laid down by Jones and Josephs (143) and Shedlovsky (144). The construction and operation of the bridge are described by Dike (145). The alternating current source employed was an audio-frequency electronic oscillator, which provided current of frequency 1000 cycles per second. A narrow-band, audio-frequency amplifier, which could be turned to the frequency of the oscillator, was used to amplify the signal from the bridge. Both the oscillator and amplifier were designed and constructed by Leeds and Northrup Company, catalog numbers 9842 and 9847 respectively. A cathode ray oscillograph type 208B (Allen B. DuMont Laboratories, Inc.) was used to determine the balance point of the bridge. The oscillator, oscillograph and amplifier were turned on 30 minutes before any resistance readings were taken. The measurements were taken by setting the bridge to a certain resistance and noting the time when the bridge became balanced.

This procedure was necessary only for rapidly changing resistances of a reaction. All resistance measurements were made to 0.1 ohm accuracy.

Conductivity cell The conductance cell used in the resistance measurements was designed by the author. A 100 ml. volumetric flask, shown in Figure 14, was fitted with two 5 square centimeter circular platinum electrodes with adjoining side arms. Mercury was used in the side arms between the electrodes and the 16 gauge copper wire leads.

Platinization and electrode pretreatment Electrodes were lightly platinized by electrolysis of a 0.025M solution of hydrochloric acid containing 0.3 per cent platinic chloride and 0.025 per cent lead acetate (146) for 20 seconds per electrode. Murr and Shiner (126) found that when a cell had been dried, e.g. for weighing, it was necessary to treat the cell with hot nitric acid before conductance measurements in order to obtain reproducible results. A similar observation was noted. The electrodes were preconditioned with a dilute sodium ethoxide solution prior to any series of measurements. Between measurements the cell was filled with absolute ethanol.

Volume of the conductance cell Volume of the conductance cell was determined gravimeterically with conductance water at 27°C. The volume was calculated for 0°C. and -24°C. using the following equation. Y is the cubical coefficient of expansion for Pyrex glass (0.0000099) (147). The

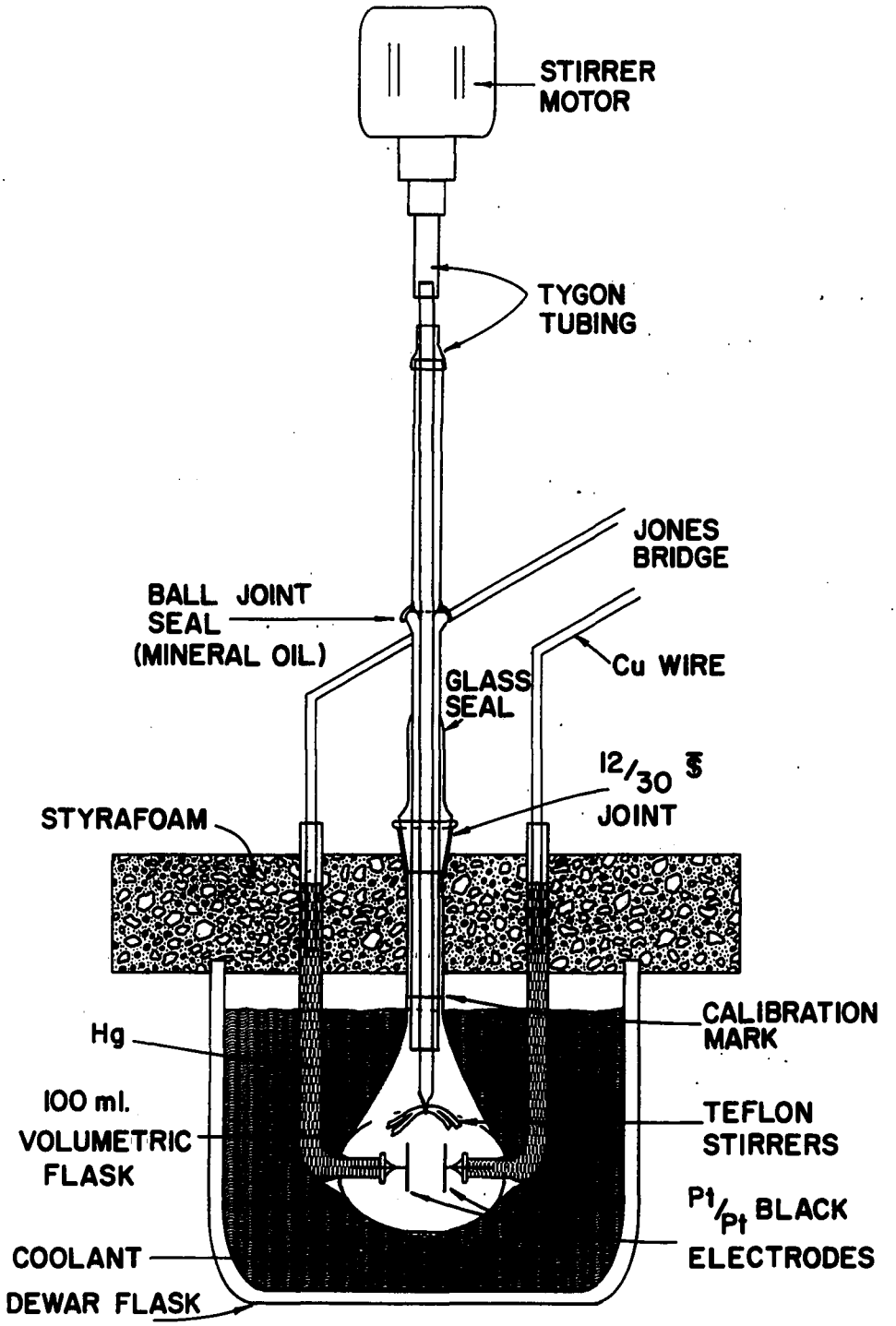


Figure 14. Conductivity cell

density of water at 27°C. is 1.00453 grams per ml. (147)

$$V' = V[1 + Y (T' - T)] \qquad (15)$$

Table 104. Volume of conductance cell at various temperatures

Temperature (°C.)	Volume of cell (ml.)
27	98.91
0	98.88
-24	98.86

Purification of materials

Absolute ethanol The absolute ethanol was used without any further purification as solvent for the eliminations reactions of the 2-carbethoxycyclopentyl p-toluenesulfonates.

1M. sodium ethoxide Freshly cut sodium (2.3 g.) was dissolved in 100 ml. of absolute ethanol under anhydrous conditions. A fresh solution was made for each series of elimination reactions.

Coolants Ice slush made from distilled water was the constant temperature bath for the kinetic experiments at 0.00°C.

Methyl chloride (Matheson Company) was the coolant at -24.22°C. The constant temperature bath was prepared by

pouring the methyl chloride from its inverted cylinder through a copper coil, which was in a dry ice-acetone bath at -30° to -35°C., and into the Dewar flask.

Anhydrous ammonia from the Matheson Company was poured directly from an inverted cylinder into the Dewar flask for a constant temperature bath at -33.35°C.

The resistance measurement for any given solution was constant over the length of any one reaction. It was concluded that the bath was at a constant temperature within limits of 0.02°C. The ice bath was checked with a platinum resistance thermometer and the fluctuations were less than 0.01°C. over 30 minutes.

Purification and analysis of sodium p-toluenesulfonate Sodium p-toluenesulfonate was prepared by Gene F. Morris by combining equimolar amounts of reagent grade p-toluenesulfonic acid and sodium hydroxide. The salt was crystallized repeatedly from 95 per cent ethanol until the pH of an aqueous solution of this sulfonate was neutral. After the salt had been dried for 24 hours at 54°C. in vacuo, no water of hydration was found by thermographic analysis. Sodium p-toluenesulfonate was found 99.6 ± 0.3 per cent pure by the following analysis.

An accurately weighed sample of sodium p-toluenesulfonate (0.2 g.) was dissolved in a minimum amount of conductance water and slowly passed through a 20 cm. column of Mallinckodt Amberlite IR-120 cationic resin in the acid form. The

sample was eluted from the column with conductance water and the eluent titrated with standard sodium hydroxide to the phenolphthalein end point.

Standardization of acid Hydrochloric acid (0.03957N) was standardized against primary standard tris-hydroxymethyaminomethane (G. F. Smith Chemical Co.). The primary standard was finely ground and dried in vacuo over anhydrous magnesium perchlorate. The normality of the acid is an average of five determinations with a relative error of less than two parts per thousand.

Standardization of base Sodium hydroxide (0.02074N) standardization was described previously on page192

Conductance water Conductance water was prepared by distilling previously distilled and deionized water from alkaline permanganate a Barnstead Water Still Model El manufactured by Barnstead Still and Sterilizer Company. The equivalent conductance of the purified water was approximately 5×10^{-7} mho and the pH was about 6.

Kinetic data

The rates of the sodium ethoxide promoted elimination reactions of the 2-carbethoxycyclopentyl p-toluenesulfonates in ethanol are reported in this thesis are of one kinetic run. These rates and other pertinent data are summarized in Tables 105 through 113. In the case of Tables 105-108 and Figures 12-14, a sample calculation is made.

Table 105. Resistance versus time on the kinetic run of trans-2-carbethoxycyclopentyl p-toluenesulfonate and sodium ethoxide/absolute ethanol at 0°C.

Time (min.)	Resistance (ohms)	Time (min.) cont.	Resistance (ohms)
3.48	stirrer started	32.19	774.0
5.33	710.0	34.64	777.0
6.56	716.0	38.27	781.0
8.00	722.0	42.43	785.0
9.35	727.0	48.50	790.0
10.00	stirrer off	56.04	795.0
11.94	734.5	65.78	800.0
13.96	740.0	103.38	810.8
16.59	746.5	122.26	813.5
19.96	754.0	149.68	815.693
21.97	758.0	159.86	816.228
23.98	761.7	201.83	817.391
25.92	765.0	225.49	817.586
28.13	768.4	248.35	817.583
29.93	771.0	259.69	817.521

Trans-2-carbethoxycyclopentyl p-toluenesulfonate was the initial reactant concentration. Excess sodium ethoxide (0.01047 moles) was found after the infinity point reading by titration with standard acid. Therefore, there was 0.02739 moles of sodium ethoxide at time zero. From this data Table 106 was experimentally constructed.

Table 106. Per cent of total resistance change versus per cent of reaction of 0.01692 molar trans-2-carbethoxycyclopentyl p-toluenesulfonate with 0.02739 molar sodium ethoxide in ethanol at 0°C.

Concentration of sodium p-toluenesulfonate (molar)	Concentration of sodium ethoxide (molar)	Resistance (R) (Ohms)	Per cent Reaction	Per cent of the total resistance change[a]
0.00000	0.02739	(Ro) 662.2	00.0	00.0
0.00376	0.02364	693.4	22.2	20.1
0.00912	0.01827	741.5	53.9	51.0
0.01283	0.01457	775.9	75.8	73.2
0.01692	0.01047	(R∞) 817.6	100.0	100.0

[a] R_T (total resistance change) = 155.4 ohms.

[$R_T = R\infty - Ro$].

The first two columns represent five synthetic solutions whose concentrations are governed by the kinetic run (see Table 105). The resistance measurements in the third column are experimental data. Per cent reaction is equal to the amount of sodium p-toluenesulfonate divided by the total amount of that salt. Per cent of the total resistance change is equal to experimental resistance minus the minimum resistance divided by the maximum resistance minus the minimum resistance minus the minimum resistance, $\left(\frac{R-Ro}{R\infty-Ro}\right)$. This data is graphed to three significant figures (Figure 13).

Table 107. Calculation of the kinetic run of trans-2-carbethoxycyclopentyl p-toluenesulfonate in sodium ethoxide/absolute ethanol at 0°C.

Time[a] (min.)	Resistance[a] (ohms)	$\frac{R-Ro}{R_T}$	% Reaction	x[b] moles of p-toluene-sulfonate reacted
5	708.5	.298	.321	0.00543
10	729.2	.431	.458	0.00775
15	742.5	.517	.545	0.00922
20	754.0	.591	.619	0.01048
25	763.4	.651	.679	0.01149
30	771.1	.701	.729	0.01234
35	777.4	.741	.768	0.01300
40	782.8	.776	.799	0.01352
45	787.3	.805	.825	0.01396
50	791.1	.830	.848	0.01435
55	794.5	.851	.867	0.01467
60	797.3	.869	.883	0.01494
65	799.6	.884	.896	0.01516
70	801.7	.898	.909	0.01538

[a]Time and resistance are taken from the graph of time vs resistance (see Table 105 and Figure 12).

[b]x = moles of reactant which has reacted as used in the integrated form of the second order rate equation.

Table 108. Calculation of the second order rate constant of the reaction of trans-2-carbethoxycyclopentyl p-toluenesulfonate in sodium ethoxide/absolute ethanol at 0°C. taking time zero as five minutes on Table 107

Time*[a] (min.)	x (molar)	$k_2 \times 10^2$ (liter $mole^{-1}$ $sec.^{-1}$)[b]
5	0.00232	3.62
10	0.00379	3.36
15	0.00504	3.36
20	0.00606	3.39
25	0.00690	3.45
30	0.00756	3.46
35	0.00809	3.45
40	0.00953	3.44
45	0.00892	3.45
50	0.00924	3.45
55	0.00951	3.45
60	0.00973	3.42
65	0.00995	3.44
Rate over entire period		3.44 ± 0.04
Rate corrected for volume of conductance cell at 0°C.		3.40 ± 0.04[c]

[a] T* = Time shown in Table 107 minus 5 minutes.

[b] a = 0.02196 molar sodium ethoxide. b = 0.01149 molar trans-2-carbethoxycyclopentyl p-toluenesulfonate. (a-b) = 0.01047 molar.

[c] Volume is corrected at this time because all previous molarities are calculated assuming the conductance cell's volume to be 100.00 ml.

Table 109. Resistance versus time of the kinetic run of trans-2-carbethoxycyclopentyl p-toluenesulfonate and sodium ethoxide/absolute ethanol at -24.22°C.

Time (min.)	Resistance (ohms)	Time (cont.)	Resistance (cont.)
4.00	stirrer on	102.87	345.0
4.75	348.3	133.55	348.4
5.53	348.9	165.06	351.3
6.50	349.4	199.10	354.2
8.35	349.8	223.63	355.8
11.00	stirrer off	263.28	358.5
11.73	344.9	379.10	366.2
14.25	345.1	452.60	369.2
19.65	344.9	514.00	371.1
23.20	344.7	586.30	373.2
34.00	343.8	617.70	373.8
44.00	343.3	683.60	375.3
70.00	344.1	703.00	375.8

The initial concentration of trans-2-carbethoxycyclopentyl p-toluenesulfonate was (0.5069 g.) 0.01623 molar. The procedure was changed for this kinetic run. A known amount of base was cooled and a cold absolute ethanol solution containing the correct amount of p-toluenesulfonate was quantitatively added to the conductance cell. The total base strength was 0.02683 molar.

After 700 minutes the reaction mixture was quenched and titrated and showed that less than 75% of the reaction had taken place.

Table 110. Per cent of total resistance change versus per cent of reaction of 0.01623 molar trans-2-carbethoxycyclopentyl p-toluenesulfonate with 0.02683 molar sodium ethoxide in ethanol at -24.22°C.

Concentration of sodium p-toluenesulfonate (molar)	Concentration of sodium ethoxide (molar)	Resistance (ohms)	Per cent Reaction	Per cent of the total resistance change[a]
0.00000	0.02683	336.4	00.0	00.0
0.00406	0.02277	345.4	25.0	14.8
0.00812	0.01871	358.5	50.0	36.7
0.001217	0.01466	376.3	75.0	65.7
0.01623	0.01060	397.1	100.0	100.0

[a] $R_\infty - R_o$ = 60.7 ohms.

Table III. Calculation of the second order rate constant of the reaction of trans-2-carbethoxycyclopentyl p-toluenesulfonate in sodium ethoxide/absolute ethanol at -24.22°C.

Time*[a] (mins.)	x (Molar)	$k_2 \times 10^{-3}$ (liter $mole^{-1}$ $sec.^{-1}$)[b]
50	0.00226	1.95
100	0.00425	2.06
150	0.00575	2.06
200	0.00701	2.07
250	0.00805	2.07
300	0.00898	2.09
350	0.00977	2.11
400	0.01037	2.08
450	0.01084	2.04
500	0.01121	1.99
550	0.01152	1.93
600	0.01178	1.88
650	0.01203	1.83
Rate over entire period		2.01 ± 0.07
Rate corrected for volume of conductance cell		1.98 ± 0.07

[a] T^* is equal to time zero in this case.

[b] $a_T^* = 0.02683$ molar

$b_T^* = 0.01623$ molar

$(a-b)_T^* = 0.0160$ molar

The initial concentration of cis-2-carbethoxycyclopentyl p-toluenesulfonate was 0.00804 molar (0.2511 grams). 0.00481 molar excess base was titrated; therefore, the initial concentration of sodium ethoxide was 0.01285 molar.

Table 112. Per cent of total resistance change versus per cent of reaction of 0.00804 molar cis-2-carbethoxycyclopentyl p-toluenesulfonate with 0.01285 molar sodium ethoxide in ethanol at -24.22°C.

Concentration of sodium p-toluenesulfonate (molar)	Concentration of sodium ethoxide (molar)	Resistance (ohms)	Per cent Reaction	Per cent of the total resistance change[b]
0.00000	0.01285	601.7	00.0	00.0
0.000201	0.01084	*[a]	25.0*[a]	14.8*[a]
0.00402	0.00883		50.0	36.7
0.00603	0.00682		75.0	65.7
0.000804	0.00481	687.0	100.0	100.0

[a]Calibration curve assumed to be similar to Table 110 and only the zero and infinity points were experimentally found.

[b]$R_\infty - R_o$ = 85.3 ohms.

Table 113. Calculation of the second order rate constant of the reaction of cis-2-carbethoxycyclopentyl p-toluenesulfonate in sodium ethoxide/absolute ethanol at -24.22°C.

Time*[a] (min.)	x (Molar)	$k_2 \times 10^{-2}$ (liter $mole^{-1}$ $sec.^{-1}$)[b]
10	0.00070	3.11
20	0.00121	2.97
30	0.00161	2.88
40	0.00194	2.83
50	0.00222	2.78
60	0.00243	2.69
70	0.00263	2.65
80	0.00279	2.60
Rate over entire period		2.81 ± 0.12
Rate corrected for volume of conductance cell		2.78 ± 0.13

[a] T^* = time zero + 20 minutes.

[b] a_T^* = 0.00935 molar

b_T^* = 0.00454 molar

$(a-b)_T^*$ = 0.00481 molar

SUMMARY

The beta elimination reaction of cis and trans-2-arylcyclopentyl p-toluenesulfonates was investigated. The rapid base-catalyzed elimination of trans-2-phenylcyclopentyl p-toluenesulfonate was shown to be cis in nature by a deuterium isotope value of 5.6 in potassium t-butoxide-t-butanol solution. The Hammett rho value (+2.77) of the cis elimination indicates that the reaction is concerted. Rho value of the trans elimination is +1.48. It was concluded that the cis elimination displays more carbanion character in the transition state than the trans elimination. The cis elimination was placed in the "central" region of the E_2 transition state spectrum.

Solvent studies concerning the cis and trans elimination of 2-arylcyclopentyl p-toluenesulfonates revealed shifts in transition state due to the combined effects of base strength and leaving group solvation. The trans elimination in sodium ethoxide-ethanol solution had a rho value of +0.99 indicating less carbanionic character in the transition state due to reduced beta proton bond breaking or a lessening of base strength. The different solvent effects in connection with cis and trans elimination reactions were attributed to the dissimilar E_2 transition states.

The p-toluenesulfonate-bromide rate ratio was studied by comparing the relative rates of cyclopentyl and p-

phenylethyl compounds. The ability of the p-toluenesulfonate moiety as a leaving group corresponds to the type of E_2 transition state the reaction processes. Cyclopentyl p-toluenesulfonate eliminates twice as fast as the bromide in potassium t-butoxide-t-butanol solution. The transition state of these reactions is "nearly E_1" in character because the beta protons are not activated by electron withdrawing groups and the secondary alpha carbon atom stabilizes positive charge more than a primary carbon atom. The bromide reacts faster in the β-phenylethyl system, an example of a "central" transition state.

An extremely rapid cis elimination is reported in which the beta protons are not acidified by a sulfone group. The beta elimination of trans-2-carbethoxycyclopentyl p-toluenesulfonate in sodium ethoxide-ethanol may be the first example of a fast E_{1CB} reaction in an all carbon system. The rates of this reaction were measured by a unique conductometric method which is suitable for very low reaction temperatures.

Synthesis and reactions of some 3-phenylcyclopentyl compounds was reported. The preliminary results seem to indicate conformational problems in the five membered ring.

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